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THE PREPARATION, CHARACTERIZATION, AND CHROMIUM(II)
REDUCTION OF PENTAAMMINECOBALT(III) COMPLEXES

by



ROBERT JAMES BALAHURA

A THESIS

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The undersigned certify that they have read, and
recommend to the Faculty of Graduate Studies for
acceptance, a thesis entitled

"THE PREPARATION, CHARACTERIZATION, AND CHROMIUM(II)
REDUCTION OF PENTAAMMINECOBALT(III) COMPLEXES"

submitted by ROBERT JAMES BALAHURA in partial fulfil-
ment of the requirements for the degree of Doctor of
Philosophy.

A B S T R A C T

The chromium(II) reduction of a series of pentaamminecobalt(III) complexes has been studied. A classification into inner- or outer-sphere paths has been made and the position of attack of the reductant on the ligand determined. The oxygen-bonded complexes of formamide, N,N-dimethylformamide, dimethylsulfoxide, and urea as well as the nitrogen bonded N-cyanoguanidine complex are reduced by means of an outer-sphere mechanism. On the other hand ligand transfer was shown to occur in the reduction of $(\text{NH}_3)_5\text{CoNHCHO}^{2+}$, $(\text{NH}_3)_5\text{CoNCNH}^{2+}$, $(\text{NH}_3)_5\text{CoO}_2\text{CNH}_2^{2+}$, $(\text{NH}_3)_5\text{CoO}_2\text{CC}_6\text{H}_4\text{CN}^{2+}$, and $(\text{NH}_3)_5\text{CoNCO}^{2+}$. Both outer- and inner-sphere paths operate in the reduction of the nitrile bonded 4-cyanophenol complex, the inner-sphere path comprising 20% of the overall reaction. For the reduction of the terephthalonitrile complex a classification into an inner- or outer-sphere path cannot be made, and an outer-sphere electron transfer to the ligand is postulated as the rate-determining step.

A large part of the work has been concerned with the characterization of the complexes and Chapter III describes the spectroscopic measurements undertaken as well as the chemical reactions of some of the complexes. The acid dissociation constant of the N isomer of formamidopentaamminecobalt(III), cyanamidopentaamminecobalt(III), and the nitrile bonded 4-cyanophenol have been determined. The protonation equilibrium constant for carbamatopentaammine-

cobalt(III) was also obtained. A kinetic study of the acid hydrolysis of isocyanatopentaamminecobalt(III) to form hexaamminecobalt(III) and carbon dioxide was carried out. The acylation of the cyanamide and 4-cyanophenol complexes was also studied.

The results of the kinetic studies of the chromium(II) reductions indicate a possible correlation between the reduction rate and the half-wave potential for the reduction of the free ligand. The studies have led to the following generalizations regarding electron transfer reactions: (1) attack of reductant at a coordinated atom does not occur, (2) the atom attached to chromium(II) in the transition state must have two lone pairs of electrons, and (3) the reducibility of the complexed ligand plays an important role in the detailed mechanism for the transfer of the electron.

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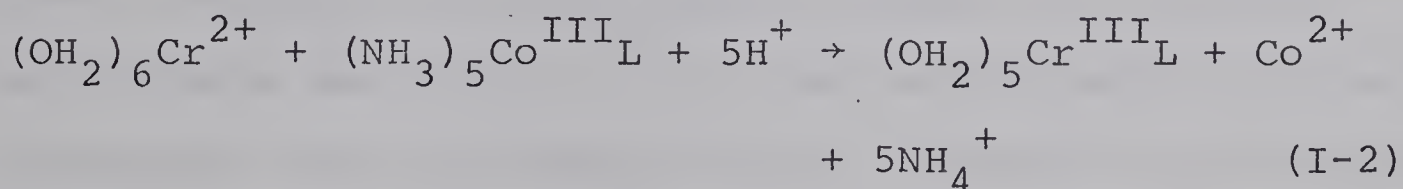
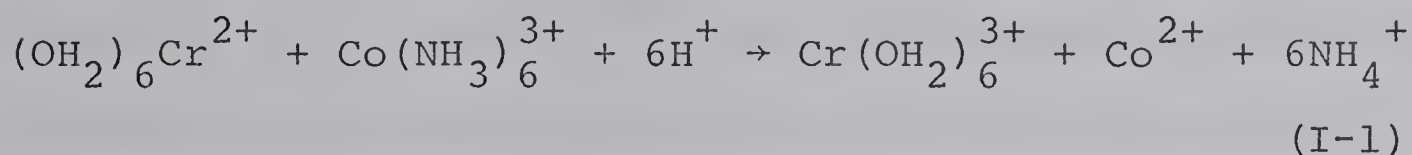
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I N T R O D U C T I O N

Chapter I

Electron transfer reactions between transition-metal complex ions have been classified into the two major categories inner-sphere and outer-sphere.¹ In the outer-sphere reaction (I-1) electron transfer takes place in an activated complex where there is no interpenetration of coordination spheres, while in an inner-sphere reaction (I-2) one or more ligands in the first coordination sphere are shared between the two reactants.



Reactions of type (I-1) are necessarily outer-sphere when the reactants are substitution-inert. In an inner-sphere reaction the bridging group is often transferred from the oxidant to the reductant and confirmation of such a transfer by an analysis of the initial products of the reaction constitutes evidence for such a mechanism. Reaction (I-2) was chosen as an example because it is ideally suited for such a product analysis since Cr^{2+} and Co^{2+} are substitution-

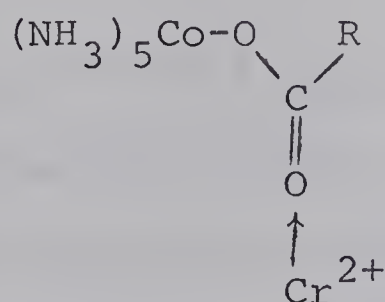
labile whereas Co^{3+} and Cr^{3+} are substitution-inert. Direct formation of $\text{Cr}(\text{OH}_2)_6^{3+}$ as the initial product is often taken to indicate an outer-sphere mechanism. Of course this assumes that an initial chromium(III) complex did not undergo a fast reaction to produce $\text{Cr}(\text{OH}_2)_6^{3+}$.

The theory of electron transfer reactions has stimulated much interest and a number of different points of view have been explored. Outer-sphere reactions have been considered by Libby,² R. J. Marcus, Zwolinski, and Eyring,^{3,4} R. A. Marcus^{5,6,7,8} and N. S. Hush.⁹ The details of the various treatments are summarized in a review by R. A. Marcus.¹⁰ For inner-sphere reactions the theoretical development is much more difficult and has been considered qualitatively by George and Griffith¹¹, and Halpern and Orgel.¹² In the latter papers four main mechanisms for the transfer of the electron are discussed: (1) double exchange - the reductant gives up an electron to the bridging group as the latter loses an electron to the oxidant; (2) superexchange - the bridging group provides vacant orbitals which serve to accept and transmit the reducing electron to the oxidant; (3) chemical exchange - (radical ion) the bridge is temporarily reduced before reduction of the oxidant; and (4) direct exchange - the bridging group serves only to bring the reactants together. Evidence supporting (2),¹³ (3),^{14,15} and (4)¹⁴ has been

presented and the individual cases will be referred to in the following sections.

The reactions of chromium(II) with carboxylatopentamminecobalt(III) complexes, $(\text{NH}_3)_5\text{CoO}_2\text{CR}^{2+}$, have been widely studied.^{16,17} The reductions are known to occur by three major paths: adjacent attack, adjacent attack with chelation, and remote attack. Examples of these will be discussed briefly.

Adjacent attack is proposed to occur through the transition state



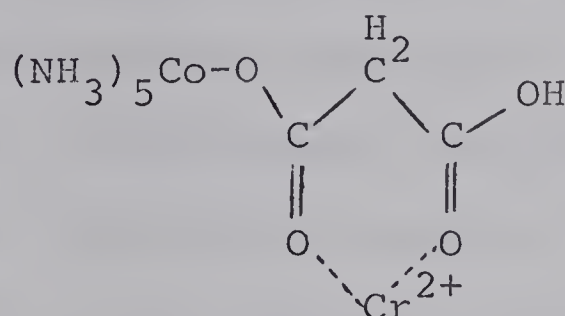
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where for example $\text{R} = \text{CH}_3, \text{H}, \text{C}_6\text{H}_5$ etc. For these reactions the enthalpy and entropy of activation generally fall in the range 8 to 9 kcal mole⁻¹ and -25 to -35 eu respectively.

The relative rates can be ascribed mainly to electronic and steric effects due to changes in the R group. There is some doubt as to which oxygen the reductant attacks for adjacent reactions. However it has been proposed¹⁸ that the reductant attacks at the oxygen bound to cobalt for the formato, acetato, chloroacetato, dichloroacetato, benzoato, and tri-

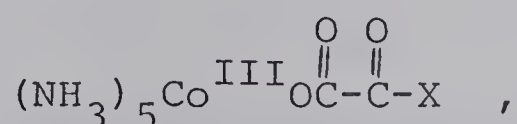
fluoroacetato complexes.

Chelation in the transition state may occur if the carboxylate has two potential donor atoms. For example with malonate as the ligand the transition state is pictured as



II

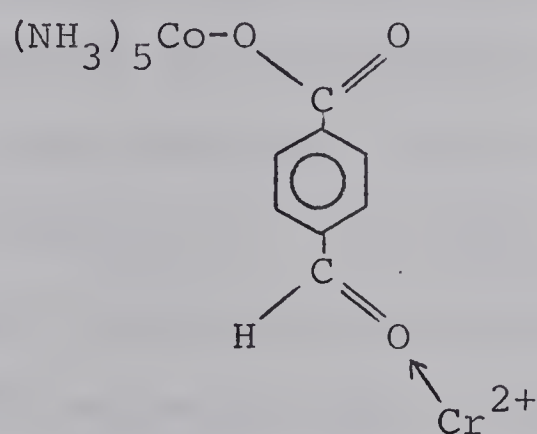
For the malonate ^{19,20,21} and glycolate ²² complexes the chelated chromium(III) product has been observed. Chelation during electron transfer for these ions is reflected in an increase in rate compared to that for adjacent attack. Price and Taube ¹³ have studied the chromium(II) reductions of a series of complexes of the class



where $\text{X} = \text{OH}, \text{O}^-, \text{NH}_2, \text{CH}_3$, or $\text{C}(\text{CH}_3)_3$, and have found chelated chromium(III) products for $\text{X} = \text{OH}, \text{O}^-$, and NH_2 . The rates for reduction are $10^2 - 10^4$ faster than for the malonate and glycolate complexes but chelation does not appear to be a primary factor for the increase in rate since the reduction of the pyruvate complex ($\text{X} = \text{CH}_3$) is about 50 times faster (at 25°) than that of the oxamate

complex ($X = \text{NH}_2$) yet the oxamate reaction leads to a stable chromium(III) chelate while the pyruvate does not. A comparison of the rates of reduction of both the complexes and the free ligands with Cr^{2+} and V^{2+} indicate that a radical ion mechanism cannot account for all the data and the authors favor a superexchange mechanism.

Remote attack, in principle, can occur for ligands having a conjugated bond system extending from a remote polar group ($\text{C} = \text{O}$ in III) to the adjacent carbonyl oxygen or, in the case of non-carboxylate ligands, to the coordinated atom.



III

There have been few well substantiated cases where remote attack actually occurs and the factors affecting remote attack are not well known. Presumably remote attack is controlled by the ability of the remote group to form a bond to the reductant and the reducibility of the ligand itself since there should be a finite time required for transfer of the electron through the ligand. In a recent study¹⁴ of the chromium(II) reduction of pentaammine-

cobalt(III) complexes of substituted pyridines the products of the reductions were fully characterized. It was shown that the nicotinamide ($3\text{-NH}_2\text{C(O)C}_5\text{H}_4\text{N}$) and isonicotinamide ($4\text{-NH}_2\text{C(O)C}_5\text{H}_4\text{N}$) complexes are reduced by remote attack at the amide carbonyl oxygen. The specific rate for reduction of the isonicotinamide complex is 500 times greater than for the nicotinamide complex and the activation parameters suggest that the two complexes are reduced by different mechanisms. Comparison of the specific rates for the chromium(II) reduction of the isonicotinamide complexes, $(\text{NH}_3)_5\text{CoNC}_5\text{H}_4\text{CONH}_2^{3+}$ ($17.4 \text{ M}^{-1} \text{ sec}^{-1}$) and $(\text{OH}_2)_5\text{CrNC}_5\text{H}_4\text{CONH}_2^{3+}$ ($1.8 \text{ M}^{-1} \text{ sec}^{-1}$) suggests that the rate determining step is transfer of an electron to the bridging ligand. For the radical ion mechanism where this is the case, replacement of $(\text{NH}_3)_5\text{Co}^{3+}$ with $(\text{OH}_2)_5\text{Cr}^{3+}$ (or $(\text{NH}_3)_5\text{Cr}^{3+}$) should not affect the electron transfer rate appreciably whereas for the direct exchange mechanism such a replacement would drastically affect the rate. On this basis the reduction of the $(\text{NH}_3)_5\text{Co}^{3+}$ complexes of CH_3CO_2^- , Cl^- , NCS^- , and F^- are inferred to be by the direct transfer mechanism. In the nicotinamide-isonicotinamide system the reducibility of the ligand should determine the effectiveness of remote attack and experimentally it is found that free isonicotinamide is reduced at least 50 times faster than nicotinamide under the same conditions.

The chromium(II) ($t_{2g}^3 e_g^1$) reduction of low spin

cobalt(III) (t_{2g}^6) to give chromium(III) (t_{2g}^3) and high spin cobalt(II) ($t_{2g}^5 e_g^2$) obviously involves considerable electronic rearrangement at the cobalt centre. It is still not known whether electron transfer occurs between the ground states or possibly between an excited electronic state of cobalt(III). For the chromium(II) reductions of pentaammineruthenium(III) complexes (t_{2g}^5) the orbital to be populated is now of π symmetry and the ligand π orbitals may be involved in the electron transfer. Stritar and Taube²³ have studied the chromium(II) reductions of a number of pentaammineruthenium(III) carboxylates $(NH_3)_5RuO_2CR^{2+}$, and have found that the rates of reduction are approximately 10^5 times greater than for the analogous cobalt(III) reductions but that the relative rates are essentially the same.

In some cases it is possible to observe the $(NH_3)_5Ru^{II}-L-Cr^{III}(OH_2)_5$ binuclear intermediate. A comparison of the rate of aquation of the intermediates bridged by OH^- and by $HCOO^-$ indicated that the metals were coordinated to different oxygens of the formate ion. If the metals were both coordinated to the same oxygen atom then the rates of hydrolysis of the intermediates should parallel the basicity of the ions, however the hydrolysis rates vary by a factor of 4 whereas formate is 10^{10} fold less basic than hydroxide. Also, since the relative effect of changing R is the same for both the Co(III) and

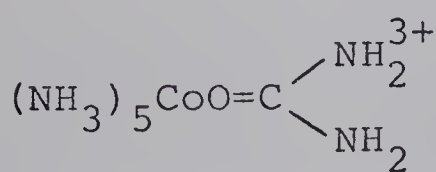
Ru(III) reactions it was concluded that the chromium(II) attacks the carbonyl oxygen in the Co(III) complexes as well.

At this point in our discussion it is appropriate to summarize the information required for a complete understanding of the mechanism of an electron transfer reaction. The first overall problem is to determine whether the reaction occurs with or without ligand transfer. If ligand transfer occurs then an inner-sphere mechanism is operative. Secondly, the detailed mechanism of the reaction must be elucidated. This entails determining the point of attack of the reductant on the ligand, obtaining a complete kinetic study of the reduction, and taking into account the stability of the initial products. Also, the detailed electronic pathway for the transfer of the electron should be determined. In practice the first two problems can be directly solved, whereas the latter is usually inferred from the data and rate comparisons for different reductants and oxidants.

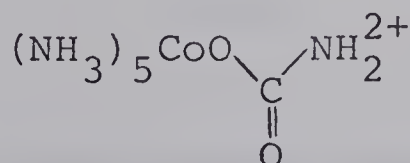
In an attempt to determine directly the point of attack of the chromium(II) on the ligand bound to cobalt(III) we have made use of the phenomenon of linkage isomerism. The nitrogen- and oxygen- bonded linkage isomers of formamidopentaamminecobalt(III), $(\text{NH}_3)_5\text{CoNH}_2\text{CHO}^{3+}$ (N isomer), and $(\text{NH}_3)_5\text{CoOCHNH}_2^{3+}$ (O isomer), as well as the conjugate base of the N isomer, $(\text{NH}_3)_5\text{CoNHCHO}^{2+}$, have been prepared.

It was expected that when these complex ions were reduced by chromium(II), if the reducing agent attacks at the ligand atom bonded to cobalt(III), then the O isomer should give an oxygen-bonded chromium(III) product, and the N isomer should give a nitrogen-bonded chromium(III) product. The opposite isomeric chromium(III) products would be expected if the chromium(II) attacks at the remote ligand atom. Unfortunately these ideal expectations have not been achieved and the N-bonded chromium(III) product has not been observed. The differences in reactions of the linkage isomers do indicate, however, that attack at the uncomplexed carbonyl oxygen occurs in the reduction of $(\text{NH}_3)_5\text{CoNHCHO}^{2+}$ but for $(\text{NH}_3)_5\text{CoOCHNH}_2^{3+}$ the reductant does not attack at the coordinated oxygen. For the latter complex no ligand transfer was observed.

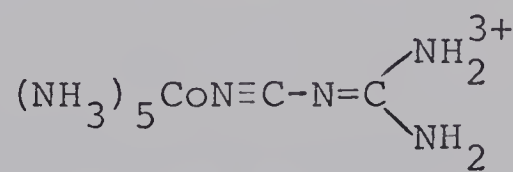
We have also studied a number of complexes with ligands which have remote NH_2 groups in order to determine the effectiveness of the NH_2 group as an electron mediator and to learn more about other specific electronic effects in electron transfer reactions. The complexes which have been studied are



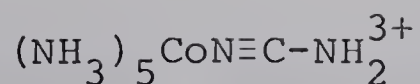
IV



V



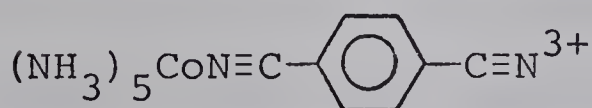
VI



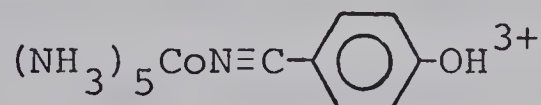
VII

The results have indicated that the NH_2 group is not capable of transmitting an electron and that attack at the atom coordinated to cobalt(III) does not occur in these systems.

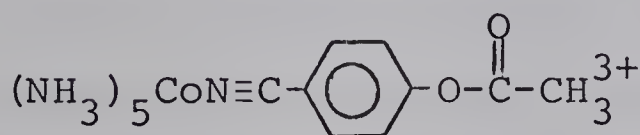
The preceding studies were extended to a number of aryl nitrile complexes (VIII-XII) and some of the factors important in remote attack (transfer of the electron across an extended conjugated system) have been determined.



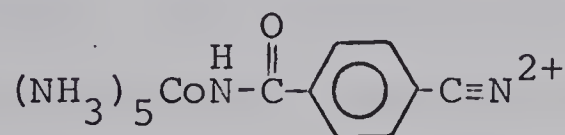
VIII



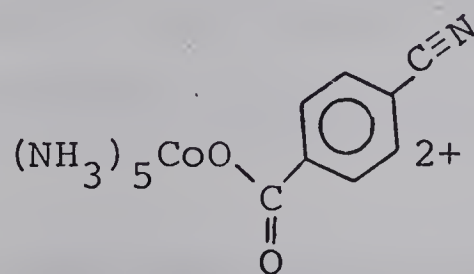
IX



X



XI



XII

The reducibility of the ligand seems to be the most important factor in determining the rate of reductions, the position of attack, and the method of the transfer of

the electron to the oxidant. Note that in the following chapters all formulae will be written as $(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{CN}$ for example where the substituents on the ring are para to each other.

In the reactions of the pentaamminecobalt(III) complexes of 4-formylbenzoate²⁴ and fumarate^{25,15} with chromium(II) the rate law contains a term first-order in hydrogen ion concentration. This term has been taken to indicate remote attack at the formyl carbonyl oxygen atom and the unbound carboxylic group respectively. Although the position of the proton in the activated complex is in doubt it has been postulated²⁶ that protonation of the adjacent carbonyl oxygen serves to improve the conjugation between the remote polar group and the bound carboxylate allowing facile electron transfer. The chromium(II) reduction of the aryl nitrile coordinated complexes are not complicated by an adjacent site for protonation or attack of chromium(II) and their study may help clear up some of the difficulties encountered with the carboxylate systems.

The studies undertaken have concentrated heavily on the characterization of the cobalt(III) complexes since in a number of cases the ligands are capable of forming linkage isomers. The structural arrangements and chemical properties of the coordinated ligands are most important in determining the mechanism of the reductions. Therefore

in a number of cases the reactions of the cobalt(III) complexes have been explored.

E X P E R I M E N T A L

Chapter II

Reagents

All solutions were prepared with water redistilled from alkaline permanganate in an all glass apparatus. Perchloric acid solutions were prepared by dilution of 70% perchloric acid (Baker and Adamson) and standardized against sodium hydroxide. The sodium hydroxide solutions were prepared by dilution of ampoules of concentrated reagent (Bio•Rad Laboratories). Lithium perchlorate solutions were prepared in two ways: (1) A weighed sample of lithium carbonate was treated with a slight excess of 70% perchloric acid, heated to remove carbon dioxide and diluted with distilled water. The excess acid was determined by titration with standard base. (2) Reagent grade lithium perchlorate (G. F. Smith Chemical Co.) was dissolved in water and filtered through a 5 micron Millipore filter (Millipore Filter Corp.) and standardized by determining the amount of hydrogen ion released from a Dowex 50-X8 ion exchange column.

Chromous perchlorate solutions were prepared by dissolving electrolytic chromium (99.999% purity, United Mineral and Chemical Corp.) in dilute perchloric acid. The chromium(II) content of the solutions was determined periodically by reacting an aliquot of the chromous solution

with an excess of standardized ferric ammonium sulfate solution. The excess ferric ion was determined by addition of potassium iodide and titration of the iodine liberated with a standard sodium thiosulfate solution. Sodium thiosulfate solutions were prepared by dilution of ampoules of concentrated reagent (Bio-Rad Laboratories).

Solutions for chromium(II) reductions were de-oxygenated either by purging with nitrogen purified by passing through two solutions of chromous chloride over zinc amalgam or with high purity Argon (Union Carbide).

All other materials were used as supplied without further purification.

Preparation of Complexes

1. Carbonatopentaamminecobalt(III) nitrate,
 $((\text{NH}_3)_5\text{CoCO}_3)(\text{NO}_3)$, and Aquopentaamminecobalt(III)
perchlorate, $((\text{NH}_3)_5\text{CoOH}_2)(\text{ClO}_4)_3$.

A solution of 225 g of powdered ammonium carbonate in 225 ml of water and 325 ml of concentrated ammonium hydroxide was added to a solution of 150 g of cobaltous nitrate in 75 ml of H_2O and 50 ml of concentrated ammonium hydroxide. The resulting mixture was air-oxidized for 24 hours. The solution was then cooled for 24 hours and the bright red crystals collected by filtration. The complex was washed thoroughly with methanol and ether and air-dried. The carbonato complex was converted to aquopentaamine-

cobalt(III) perchlorate by adding the solid directly to warm 1.0M HClO_4 . The solution was cooled and the crystals collected by filtration. The aquo compound was recrystallized twice from 1.0M HClO_4 to remove all traces of nitrate.

2. The Conjugate Base of the N-isomer of Formamidopentamminecobalt(III) perchlorate, $((\text{NH}_3)_5\text{CONHCHO})(\text{ClO}_4)_2$.

The conjugate base of the N-isomer of formamidopentamminecobalt(III) perchlorate was prepared by dissolving 20 g of aquopentamminecobalt(III) perchlorate in 100 ml of reagent grade formamide and heating the solution on a steam bath for 4 hours. The resulting solution was mixed with approximately 300 ml of sec-butyl alcohol and the resulting precipitate of $((\text{NH}_3)_5\text{CONHCHO})(\text{ClO}_4)_2$ was collected by filtration, washed with ethanol and ether, and air-dried. Addition of more sec-butyl alcohol to the filtrate from above precipitates a pink crystalline material which will be described under preparation 15. The conjugate base was recrystallized three times from water. The absorption spectrum shows maxima at 250 nm (ϵ , 25,200), 348 nm (ϵ , 81.3), and 484 nm (ϵ , 68.4). In 1.0M perchloric acid the protonated species $((\text{NH}_3)_5\text{CONH}_2\text{CHO})(\text{ClO}_4)_3$ predominates and shows absorption maxima at 340 nm (ϵ , 58.2) and 478 nm (ϵ , 62.2).

The $((\text{NH}_3)_5\text{CONH}_2\text{CHO})(\text{ClO}_4)_3$ species is easily precipitated from water with perchloric acid but is not readily obtained in pure solid form. It was found that washing the

solid with 98% ethanol caused removal of a proton and yielded a mixture of the N-bound forms. The acid form of the N isomer also isomerizes to the oxygen isomer in the solid state.

Titration of a carefully purified sample of $((\text{NH}_3)_5\text{CoNH}_2\text{CHO})(\text{ClO}_4)_3$ with standard sodium hydroxide gave an equivalent weight of 493, compared to the calculated value of 487.5.

Anal. Calcd for $((\text{NH}_3)_5\text{CoNHCHO})(\text{ClO}_4)_2$: C, 3.10; H, 4.43; N, 21.7. Found: C, 3.25; H, 4.43; N, 21.3.

3. Oxygen-Bonded Formamidopentaamminecobalt(III) perchlorate, $((\text{NH}_3)_5\text{CoOCHNH}_2)(\text{ClO}_4)_3$.

The oxygen-bonded isomer was prepared through the intermediate trimethylphosphatopentaamminecobalt(III) complex. The method used in this preparation is based on the assumption that the O isomer forms first in formamide and then isomerizes with release of a proton to $(\text{NH}_3)_5\text{CoNHCHO}^{2+}$. Thus mild conditions would be necessary to prepare the O isomer. 20 g of aquopentaamminecobalt(III) perchlorate was dissolved in 200 ml of trimethylphosphate with Linde molecular sieves and the solution heated for 2 hours on a steam bath. Then the excess trimethylphosphate was extracted with t-butyl alcohol leaving an oil of the trimethylphosphatopentaamminecobalt(III) perchlorate. This oil was dissolved in 125 ml of formamide and the solution was allowed to stand

at ambient temperature for 2 hours. Addition of sec-butyl alcohol to this solution gave a precipitate which contained a mixture of products. This mixture was separated by cation exchange chromatography on Rexyn 102(H) (Fisher Scientific Co.) in the sodium ion form, eluting with solutions of NaHCO_3 , adjusted to pH 7.2, in increasing concentrations up to 1.0M. This procedure gave a separation into three bands, the most strongly held being the O isomer of formamidopentaamminecobalt(III). Rather than eluting the complex from the column, it was found to be more efficient to separate the bands on the ion exchange resin physically. The resin was washed with water and then treated in a batch with enough concentrated perchloric acid to remove the complex. This process also released a considerable amount of water from the resin. The resin was removed from the solution containing the complex by filtration, and the complex precipitated by adding sodium perchlorate to the filtrate.

The visible absorption spectrum showed maxima at 346 nm (ϵ , 57.5) and 502 nm (ϵ , 68.8) in water and 1.0 M perchloric acid.

Anal. Calcd for $((\text{NH}_3)_5\text{CoOCHNH}_2)(\text{ClO}_4)_3$: C, 2.47; H, 3.73; N, 17.3. Found: C, 2.52; H, 4.10; N, 16.9.

4. N,N-Dimethylformamidopentaamminecobalt(III) perchlorate, $((\text{NH}_3)_5\text{CoOCHN}(\text{CH}_3)_2)(\text{ClO}_4)_3$.

The complex was prepared by heating 20 g of aquopenta-

amminecobalt(III) perchlorate in 200 ml of N,N-dimethylformamide for 3 hours on a steam bath. The product was precipitated from the reaction solution by adding sec-butyl alcohol. The complex was recrystallized five times by dissolving it in the minimum amount of water at $\sim 50^\circ$, filtering the solution, and then cooling to $\sim 5^\circ$. The product was collected by filtration and washed in the usual way with 95% ethanol and ether. The visible absorption spectrum showed maxima at 347 nm (ϵ , 66.7) and 506 nm (ϵ , 77.3). Gould²⁷ has reported maxima at 347 nm (ϵ , 62.5) and 505 nm (ϵ , 76.0).

Anal. Calcd for $((\text{NH}_3)_5\text{CoOCHN}(\text{CH}_3)_2)(\text{ClO}_4)_3$: C, 7.00; H, 4.32; N, 16.3. Found: C, 7.56; H, 4.37; N, 16.2.

5. Oxygen-Bonded Urea, $((\text{NH}_3)_5\text{CoOC}(\text{NH}_2)_2)(\text{ClO}_4)_3$.

12 g of $((\text{NH}_3)_5\text{CoOH}_2)(\text{ClO}_4)_3$ and 15 g of urea were dissolved in 100 ml of N,N-dimethylacetamide over 5 g of molecular sieves. The mixture was heated on a steam bath for one hour and the crude product was isolated by adding ~ 800 ml of sec-butyl alcohol. The product was filtered and washed with ethanol and ether and air-dried. Fractional recrystallization from warm water containing sodium perchlorate yielded two complexes, the isocyanato complex described in preparation 6 and the O-bonded urea compound. The perchlorate salt of the latter is much more soluble in water. The O-bonded urea complex was purified by further

recrystallization and also by cation exchange chromatography as described previously, using sodium chloride as the eluting agent. The properties of the complex purified by both methods were identical. The extinction coefficients obtained from both methods agreed within 3-5%. The visible spectrum of the urea complex purified by ion exchange shows maxima at 347 nm (ϵ , 54.2) and 514 nm (ϵ , 67.4).

Anal. Calcd for $((\text{NH}_3)_5\text{CoOC}(\text{NH}_2)_2)(\text{ClO}_4)_3$: C, 2.39; H, 3.79; N, 19.5. Found: C, 2.39; H, 3.74; N, 19.2.

6. Cyanatopentaamminecobalt(III) perchlorate,



The cyanatopentaamminecobalt(III) perchlorate complex was prepared by a number of different synthetic routes.

- (a) 10 g of $((\text{NH}_3)_5\text{CoOH}_2)(\text{ClO}_4)_3$ and 10 g of either urea or methylurea or phenylurea was dissolved in 80 ml of trimethylphosphate over ~5 g of Linde molecular sieves. The mixture was heated on the steam bath for one hour during which time the solution changed from orangish-red to reddish-purple. The solution was cooled and the product precipitated by the addition of ~500 ml of sec-butyl alcohol. The product was collected by filtration and recrystallized from warm water (40-50°) containing a small amount of sodium perchlorate.

The product was a red crystalline compound. The

visible spectrum exhibited peaks at 353 nm (ϵ , 84.8) and 501 nm (ϵ , 130). From the preparation using phenylurea the visible spectrum showed peaks at 353 nm (ϵ , 77.6) and 501 nm (ϵ , 120) indicating the presence of an impurity. The impurity was removed by cation exchange chromatography on Rexyn 102(H) in the sodium ion form eluting with sodium acetate in increasing concentrations up to 0.5M. This procedure gave two bands, one which moved down the column like a 1+ ion and the cyanato complex which moved slightly with 0.3M sodium acetate. The cyanato band was separated from the impurity band physically and the complex removed from the resin in a batch by five treatments with 50 ml of 1.5M sodium perchlorate. After filtration of the resin the complex was precipitated by the addition of solid sodium perchlorate. The visible spectrum of the purified complex showed peaks at 353 nm (ϵ , 82.6) and 501 nm (ϵ , 128).

- (b) 10 g of $((\text{NH}_3)_5\text{CoOH}_2)(\text{ClO}_4)_3$ was dissolved in molten urea (approximately 50 g) at 135-136° and stirred for 3 hours in the presence of 5 g of Linde molecular sieves. The reaction mixture was cooled and the urea extracted with sec-butyl alcohol. The product was precipitated by the alcohol and was collected by filtration and recrystallized four times from dilute

aqueous sodium perchlorate. The resulting complex had the same properties as that from (a) except that the extinction coefficients indicated that a small amount of an impurity was present. The visible spectrum had peaks at 353 nm (ϵ , 79.0) and 501 nm (ϵ , 119).

- (c) $((\text{NH}_3)_5\text{CoOP}(\text{OCH}_3)_3)(\text{BF}_4)_3$ was prepared by heating $((\text{NH}_3)_5\text{CoOH}_2)(\text{BF}_4)_3$ in trimethylphosphate, over Linde molecular sieves, for one hour on a steam bath. The product was precipitated by adding ether and sec-butyl alcohol, and was used without further purification. $((\text{NH}_3)_5\text{CoOH}_2)(\text{BF}_4)_3$ was prepared by addition of 50% HBF_4 to an aqueous solution of the corresponding perchlorate salt and recrystallized twice from dilute aqueous HBF_4 .) The trimethylphosphato product was dissolved in molten urethane (approximately 30 g) at about 65° and stirred for 5 hours, in the presence of 1-2 g of Linde molecular sieves. The urethane was then extracted in 98% ethanol (200 ml) and the complex filtered off. The crude product was recrystallized as in (a) and gave a complex with identical properties to those of the product from (a). The visible spectrum showed peaks at 353 nm (ϵ , 83.4) and 501 nm (ϵ , 128).

- (d) The same procedure as in (a) was used except that

N,N-dimethylacetamide was substituted for urea. This preparation yielded the cyanato complex after fractional crystallization as described in preparation 5. The visible spectrum showed maxima at 353 nm (ϵ , 84.3) and 501 nm (ϵ , 131).

Very similar analyses were obtained from (a), (c), and (d). A typical analysis is given. Calcd: C, 3.12; H, 3.90; N, 21.8. Found: C, 3.23; H, 4.02; N, 21.7. From (b) Found: C, 3.19; H, 4.08; N, 22.8.

7. Carbamatopentaamminecobalt(III) perchlorate,

$$\frac{((\text{NH}_3)_5\text{CoO}_2\text{CNH}_2)(\text{ClO}_4)_2}{2}$$

The carbamatopentaamminecobalt(III) complex was prepared according to the method described by Sargeson and Taube²⁸, except that aquopentaamminecobalt(III) nitrate and potassium cyanate were used instead of the perchlorate salt of the complex and sodium cyanate. The resulting complex was recrystallized three times by dissolution in a minimum volume of warm water (~50°), followed by addition to an equal volume of a saturated sodium perchlorate solution. This insured that all the nitrate was replaced by perchlorate, as confirmed by the absence of NO_3^- peaks in the infrared spectrum. In 1.0M LiClO_4 the visible spectrum of the complex shows peaks at 353 nm (ϵ , 61.8) and 505 nm (ϵ , 77.9). In 1.0M HClO_4 a protonated species predominates which shows absorption maxima at 349 nm (ϵ , 51.8)

and 507 nm (ϵ , 67.4).

Anal. Calcd for $((\text{NH}_3)_5\text{CoO}_2\text{CNH}_2)(\text{ClO}_4)_2$: C, 2.98; H, 4.25; N, 20.8. Found: C, 3.18; H, 4.33; N, 20.6.

8. N-cyanoguanidine Complex, $((\text{NH}_3)_5\text{CoNCNC}(\text{NH}_2)_2)(\text{ClO}_4)_3$

Cyanamide²⁹, H_2NCN , is extremely sensitive to heat and will polymerize violently at temperatures above its melting point (40°C). Solutions of cyanamide are very sensitive to traces of alkali which cause dimerization to N-cyanoguanidine. (The common name of this compound is "dicyandiamide", however as pointed out by Fieser³⁰ N-cyanoguanidine is the correct name.) The sample of cyanamide used in this preparation had stood for two years at room temperature. It was completely fused in the bottle and was probably all in the dimeric state. This was subsequently confirmed by ir and nmr spectra.

15 g of cyanamide (Eastman Organic Chemicals), which was mostly N-cyanoguanidine as noted above, 15 g of aquo-pentaamminecobalt(III) perchlorate, 10 g of Linde 5A molecular sieves, and ~100 ml of solvent trimethylphosphate were heated for one hour on a steam bath. During this time the solution changed from orange-red to deep red to bright orange in color. The solution was cooled and filtered from the molecular sieves and the complex precipitated with ~1000 ml of sec-butyl alcohol. The complex was recrystallized three times by dissolution in warm water and

addition of solid sodium perchlorate. The visible absorption spectrum showed maxima at 266 nm (ϵ , 1710), 348 nm (ϵ , 123), and 487 nm (ϵ , 116) in water and 1.0M HClO_4 .

Anal. Calcd for $((\text{NH}_3)_5\text{CoNCNC}(\text{NH}_2)_2)(\text{ClO}_4)_3$: C, 4.56; H, 3.61; N, 23.9. Found: C, 4.92; H, 3.85; N, 24.0.

9. Cyanamidopentaamminecobalt(III) Perchlorate,
 $((\text{NH}_3)_5\text{CoNCNH}_2)(\text{ClO}_4)_3$.

The ligand used was supplied by Cyanamid of Canada as Aero Cyanamide-100 in the form of pellets and kept refrigerated at all times. In a typical preparation 25 g of cyanamide pellets, 15 g of aquopentaamminecobalt(III) perchlorate, and 20 g of Linde 3A molecular sieves was mixed with 150-200 ml of N,N-dimethylacetamide and heated on a steam bath for one hour. The resulting orange-red solution was cooled, filtered, and 1500 ml of sec-butyl alcohol added to precipitate the complex. Trimethylphosphate was also used as solvent with the same results. The crude complex was first recrystallized from warm water yielding two main fractions. The least soluble fraction was a mixture of the N-cyanoguanidine complex and as yet an uncharacterized compound, while the soluble fraction contained the desired cyanamide complex along with ~10% impurity of the N-cyanoguanidine complex and the unknown complex. Fractional recrystallization of this latter mixture nine times finally yielded the cyanamide complex in ~95% purity, the remaining 5% being the N-cyanoguanidine

complex. In 1.0M perchloric acid the visible absorption spectrum shows peaks at 339 nm (ϵ , 65.3) and 480 nm (ϵ , 73.7) whereas in water the maxima are at 304 nm (ϵ , 347) and 486 nm (ϵ , 77.1). In 1.0M sodium acetate the visible absorption showed maxima at 304 nm (ϵ , 965) and 521 nm (ϵ , 108).

Anal. Calcd for $((\text{NH}_3)_5\text{CoNCCNH}_2)(\text{ClO}_4)_3$: C, 2.48; H, 3.51; N, 20.2. Found: C, 2.41; H, 3.54; N, 20.0.

10. Terephthalonitrile Complex, $((\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{CN})(\text{ClO}_4)_3$.

15 g of terephthalonitrile, 20 g of aquopentaammine-cobalt(III) perchlorate, and 20 g of Linde 3A molecular sieves were mixed with 200 ml of trimethylphosphate and heated on a steam bath for 3 hours. The orange solution was cooled, filtered, and added to 800 ml of sec-butyl alcohol which precipitated some of the complex and caused the remainder to come out as an oil. Stirring with more sec-butyl alcohol converted the oil to the solid compound. The complex was filtered and then slurried in methanol for 24 hours to remove any trimethylphosphato complex formed during the reaction. The complex was filtered and recrystallized from warm water with added sodium perchlorate. The compound was bright yellow in color. The visible absorption spectrum in H_2O showed maxima at 244 nm (ϵ , 2.33×10^4), 255 nm (ϵ , 1.89×10^4), 329 nm (ϵ , 86.5), and 469 nm (ϵ , 78.5).

Anal. Calcd for $((\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{CN})(\text{ClO}_4)_3$: C, 16.8; H, 3.33; N, 17.2. Found: C, 16.9; H, 3.29; N, 17.3.

In an attempt to remove a suspected impurity from the above complex the compound was subjected to cation exchange chromatography on Rexyn 102(H) weak acid resin using sodium acetate as the eluting agent. The terephthalonitrile complex was successfully removed from a small amount of compound which was held more strongly; this could be the symmetrical dimer. However, an orange fraction was eluted in a diffuse band from the terephthalonitrile complex fraction. This orange fraction seemed to come directly from the terephthalonitrile band and the latter fraction was slowly depleted in quantity. The new band had elution characteristics of a 2+ ion and could be eluted with 0.3—0.4M sodium acetate. This fraction was subsequently collected and precipitated from solution by the addition of concentrated HClO_4 or solid sodium perchlorate. The orange solid, which was subsequently found to be $((\text{NH}_3)_5\text{CoNHC}(\text{O})\text{C}_6\text{H}_4\text{CN})(\text{ClO}_4)_2$, had a visible spectrum that showed maxima at 235 nm (ϵ , 2.41×10^4), 345 nm (ϵ , 117), and 484 nm (ϵ , 83.2) in H_2O . In 1.0M perchloric acid the maxima occurred at 235 nm (ϵ , 2.13×10^4), 342 nm (ϵ , 87.6), and 478 nm (ϵ , 73.5).

Anal. Calcd for $((\text{NH}_3)_5\text{CoNHC}(\text{O})\text{C}_6\text{H}_4\text{CN})(\text{ClO}_4)_2$: C, 19.7; H, 4.10; N, 20.1. Found: C, 19.6; H, 4.36; N, 20.3.

11. 4-Cyanophenol Complex, $((\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{OH})(\text{ClO}_4)_3$:

18 g of 4-cyanophenol, 10 g of aquopentaamminecobalt(III), and 30 g of Linde 3A molecular sieves were mixed with 120 ml of trimethylphosphate and heated on a steam bath for 45 minutes. The yellow-brown solution was then cooled, filtered and treated with 900 ml of sec-butyl alcohol. The precipitate which formed was collected by filtration and recrystallized from warm water and dilute HClO_4 . The freshly recrystallized complex was a bright yellow crystalline material. It was found that the solid partially decomposed at room temperature over a period of one week. During this time the yellow color changed to a yellowish brown, and a phenolic odor was detectable.

The freshly recrystallized complex had a visible-ultraviolet absorption spectrum in H_2O that showed maxima at 295 nm (ϵ , 2.32×10^4) and 473 nm (ϵ , 108). In 1.0M HClO_4 the maxima occurred at 257 nm (ϵ , 2.16×10^4) and 472 nm (ϵ , 95.5). Titration of a weighed sample of the complex with standard base gave an equivalent weight of 567 compared to the theoretical value of 561.6.

Anal. Calcd for $((\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{OH})(\text{ClO}_4)_3$: C, 15.0; H, 3.56; N, 15.0. Found: C, 15.0; H, 3.46; N, 14.8.

12. 4-Cyanobenzoatopentaamminecobalt(III) perchlorate,
 $((\text{NH}_3)_5\text{CoO}_2\text{CC}_6\text{H}_4\text{CN})(\text{ClO}_4)_2$:

10.5 g of sodium 4-cyanobenzoate, 5 g of 4-cyano-

benzoic acid, and 10 g of aquopentaamminecobalt(III) perchlorate were dissolved in 75 ml of N,N-dimethylformamide in the presence of Linde molecular sieves and heated on a steam bath for 2.5 hours with stirring. The solution was cooled, filtered, and sec-butyl alcohol added to precipitate the complex. The complex was filtered and recrystallized by dissolving in a warm ($\sim 50^\circ$) solution of dilute HCl, filtering, and adding concentrated HClO_4 to precipitate the complex. The complex was then purified by cation exchange chromatography on Rexyn 102(H) weak acid resin in the sodium ion form. The separation was achieved by moving the 4-cyanobenzoate down the column with 0.3-0.4M sodium acetate after which the desired band was separated physically from the column. The complex was freed from the resin as described in preparation 3. The chromatographed complex had a visible absorption spectrum which had maxima at 242 nm (ϵ , 3.05×10^4), 349 nm (ϵ , 69.0), and 503 nm (ϵ , 82.0) in H_2O and 1.0M HClO_4 .

Anal. Calcd for $((\text{NH}_3)_5\text{CoO}_2\text{CC}_6\text{H}_4\text{CN})(\text{ClO}_4)_2$: C, 19.6; H, 3.89; N, 17.2. Found: C, 19.6; H, 4.12; N, 16.6.

13. The Conjugate Base of the Nitrogen Isomer of Acetamide,
 $((\text{NH}_3)_5\text{CoNHC}(\text{CH}_3)\text{O})(\text{ClO}_4)_2$.

This complex was prepared by using both trimethylphosphate and molten acetamide as solvent. In a representative preparation 20 g of aquopentaamminecobalt(III) per-

chlorate and 40 g of acetamide were dissolved in trimethylphosphate (or the solvent TMP was omitted) in the presence of Linde molecular sieves and heated on a steam bath for 4 hours. The complex was precipitated from solution with excess sec-butyl alcohol and recrystallized from warm water by adding sodium perchlorate solution. Both preparations gave a mixture of products. The desired compound was obtained by cation exchange chromatography on Rexyn 102(H) weak acid resin in the hydrogen ion form. The complex was moved down the column with 0.3M sodium acetate and treated as described previously in preparation 3. The visible absorption spectrum in water shows maxima at 351 nm (ϵ , 83.5) and 486 nm (ϵ , 71.1). In 1.0M perchloric acid a protonated species predominates and has a maxima at 341 nm (ϵ , 57.5) and 477 nm (ϵ , 61.5).

Anal. Calcd for $((\text{NH}_3)_5\text{CoNHC}(\text{CH}_3)\text{O})(\text{ClO}_4)_2$: C, 6.00; H, 4.74; N, 21.0. Found: C, 6.08; H, 4.75; N, 20.9.

14. N-methylformamidopentaamminecobalt(III) perchlorate,
 $((\text{NH}_3)_5\text{CoOCHNH}(\text{CH}_3))(\text{ClO}_4)_3$.

20 g of aquopentaamminecobalt(III) perchlorate was dissolved in 100 ml of N-methylformamide in the presence of Linde molecular sieves and heated on a steam bath for 3 hours. The solution was cooled, filtered, and the complex precipitated with 500 ml of sec-butyl alcohol. The compound was recrystallized from warm water by adding solid

NaClO_4 . The complex was purified by cation exchange chromatography on Rexyn 102(H) weak acid resin in the sodium ion form. The eluting agent was sodium acetate increasing in concentration to 1.0M. This separated the complex from aquopentaamminecobalt(III) which is held more strongly. The complex was recovered as described previously in preparation 3. The visible absorption spectrum showed maxima at 345 nm (ϵ , 66.6) and 504 nm (ϵ , 72.5) in H_2O .

Anal. Calcd for $((\text{NH}_3)_5\text{CoOCHNH}(\text{CH}_3))(\text{ClO}_4)_3$: C, 4.79; H, 4.00; N, 16.7. Found: C, 4.70; H, 3.99; N, 16.5.

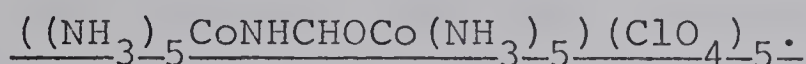
15. Dimethylsulfoxidopentaamminecobalt(III) perchlorate,
 $((\text{NH}_3)_5\text{CoOS}(\text{CH}_3)_2)(\text{ClO}_4)_3$.

15 g of aquopentaamminecobalt(III) perchlorate was dissolved in approximately 100 ml of dimethylsulfoxide (DMSO) with 20 g of Linde molecular sieves and heated on a steam bath for 2 hours. The resulting solution was cooled, filtered, and 800 ml of sec-butyl alcohol added to precipitate the complex. The compound was recrystallized from warm water by adding solid sodium perchlorate. The complex was purified by cation exchange chromatography on Rexyn 102(H) weak acid resin in the sodium ion form. Elution with sodium acetate increasing in concentration to 1.0M gave a separation into two bands the least strongly held being the desired DMSO complex. The latter was re-

covered as described previously in preparation 3. The visible absorption spectrum showed maxima at 346 nm (ϵ , 56.9) and 517 nm (ϵ , 54.5) in H_2O .

Anal. Calcd for $((\text{NH}_3)_5\text{CoOS}(\text{CH}_3)_2)(\text{ClO}_4)_3$: C, 4.61; H, 4.03; N, 13.4; S, 6.15. Found: C, 4.50; H, 4.28; N, 13.3; S, 5.68.

16. A New Dinuclear Cobalt Complex,



In the preparation of the conjugate base of the nitrogen isomer of formamidopentaamminecobalt(III) perchlorate an unknown pink crystalline material was isolated. This complex was also obtained by reaction of 2.5 g of aquopentaamminecobalt(III) perchlorate with 2.1 g of $((\text{NH}_3)_5\text{CoNHCHO})(\text{ClO}_4)_2$ in 50 ml of trimethylphosphate over 5 g of Linde molecular sieves for 3 hours on a steam bath. In both cases the complex was purified by cation exchange chromatography on Rexyn 102(H) weak acid resin in the sodium ion form. Elution was carried out with increasing concentrations of sodium acetate up to 2.0M. All impurities were eluted from the column with this concentration of eluting agent and the dimer remained at the top of the column. The visible absorption spectrum showed maxima at 341 nm (ϵ , 164) and 492 nm (ϵ , 141) in H_2O . The complex was quantitatively insoluble in either 1.0M LiClO_4 or HClO_4 at room temperature.

Anal. Calcd for $((\text{NH}_3)_5\text{CoNHCHOCO}(\text{NH}_3)_5)(\text{ClO}_4)_5$: C, 1.45;

H, 3.86; N, 18.6. Found: C, 1.75; H, 3.86; N, 18.3.

Kinetic Measurements.

The spectrophotometer cell and reagent solution containers were all sealed with rubber serum caps and flushed with deoxygenated nitrogen or high purity argon. Reagents were all handled and mixed using standard syringe techniques.

For reactions run under pseudo-first-order conditions (reductant in a 15-20 fold excess over oxidant) the observed rate constant was determined from the slope of a plot of $\log (A_t - A_\infty)$ vs. time, where A_t and A_∞ are the absorbancies at time t and after the reaction is complete. For reactions followed under second order conditions (the ratio of reductant to oxidant $< 10:1$) the rate constant was determined from a plot of

$$\log \left[1 - \left(1 - \frac{b}{a} \right) \left(\frac{A_o - A_\infty}{A_t - A_\infty} \right) \right] \text{ vs. time ,}$$

which has a slope equal to $2.303 k_2 / (b-a)$. A_o , A_∞ , A_t and k_2 have the usual meanings and b is the initial reductant concentration and a is the initial oxidant concentration.

The activation parameters were determined using the transition state equation ³¹

$$\log \left(\frac{k}{T} \right) = - \frac{\Delta H^\ddagger}{2.303R} \left(\frac{1}{T} \right) + \left\{ \frac{\Delta S^\ddagger}{2.303R} + \log \left(\frac{k k_B}{h} \right) \right\}$$

where k is the specific rate constant, k_B is Boltzmann's

constant, κ is the transmission coefficient, h is Planck's constant, T is the temperature in $^{\circ}\text{K}$, R is the gas constant in $\text{cal deg}^{-1} \text{mole}^{-1}$, ΔH^{\ddagger} is the enthalpy of activation, and ΔS^{\ddagger} is the entropy of activation. A plot of $\log(k/T)$ versus T^{-1} should be a straight line with slope $-\Delta H^{\ddagger}/2.303R$ and intercept $[\Delta S^{\ddagger}/2.303R + \log(k_B/h)]$ where κ is assumed to be unity, (adiabatic transfer).

The extent of reaction was determined from the decrease in absorbance with time of the high wavelength peak of the cobalt(III) complex. The rates at 25.5° for the reduction of the conjugate base of the nitrogen isomer of formamidopentaamminecobalt(III) perchlorate were measured using a Cary Model 14 spectrophotometer. All other rates were determined using Bausch and Lomb 505 and Precision spectrophotometers.

The temperature of the reaction solution in the spectrophotometer cell was controlled by pumping water from a Colara constant temperature bath through a specially bored aluminum cell holder. The temperature of the bath was regulated by a Fisher Thermistemp controller, with the thermistor probe inserted in the cell holder next to the spectrophotometer cell. The temperature inside the cell was periodically checked with a thermometer and also several times with a thermocouple.

Stoichiometry

The stoichiometries of the chromium(II) reductions

were determined by analyzing for the chromium(II) left after ten half-times for reaction solutions containing various initial chromium(II) to cobalt(III) ratios. The analysis was carried out by oxidation of chromium(II) with excess iron(III) and determining the excess iron(III) iodometrically.

Also, for a number of complexes the visible absorption spectrum was scanned for initial ratios of reductant to oxidant of 1:1 and the disappearance of all the cobalt(III) noted.

Ion Exchange Separation of Reaction Mixtures.

Reaction mixtures from kinetic runs and from reactions carried out at Cr(II):Co(III) ratios between 1:1 and 10:1 were ion-exchanged at 5° using Dowex 50W-X12 cation exchange resin. The resin was pretreated with 30% HClO₄, distilled water, 50% acetone, ethanol, and distilled water in order to remove all traces of organic material. Elution was carried out using a standard 0.5M NaClO₄, 0.1M HClO₄ solution. The eluting solution was generally added in one-quarter strength and the concentration gradually increased as separation was achieved. Under optimum conditions the total time spent on the ion exchange column was about 90 minutes.

All products were characterized spectrophotometrically on a Cary Model 14 spectrophotometer. The extinction coefficients were calculated on the basis of the chromium

concentration which was determined spectrophotometrically as chromate. The oxidation of the chromium(III) species was carried out in basic solution (final solution 1.0M in NaOH, 500 ml volumetric flask) with hydrogen peroxide. The chromium concentration was determined from the absorbance at 372 nm where the extinction coefficient is $4.815 \times 10^3 \text{ l mole}^{-1} \text{ cm}^{-1}$.

Determination of Ionization Constants.

The equilibrium constant for the proton dissociation from $(\text{NH}_3)_5\text{CoNH}_2\text{CHO}^{3+}$ to give $(\text{NH}_3)_5\text{CoNHCHO}^{2+}$ was determined spectrophotometrically at 25.5°, 34.6°, and 44.4° at a wavelength of 318 nm. Varying amounts of standardized perchloric acid solution were added to solutions of $(\text{NH}_3)_5\text{CoNHCHO}(\text{ClO}_4)_2$ and lithium perchlorate (to adjust the ionic strength to 0.92M).

The dissociation constant for the reaction of $(\text{NH}_3)_5\text{CoO}_2\text{CNH}_3^{3+}$ to give $(\text{NH}_3)_5\text{CoO}_2\text{CNH}_2^{2+}$ was also determined spectrophotometrically at 25.8° and at a wavelength of 290 nm. Varying amounts of standard HClO_4 and LiClO_4 were added to solutions of $(\text{NH}_3)_5\text{CoO}_2\text{CNH}_2^{2+}$ (to adjust the ionic strength to 1.0M).

The spectra were determined using a Bausch and Lomb 505 spectrophotometer fitted with a standard thermostated cell compartment. The method and treatment of data followed that outlined by Albert and Sergeant.³³

The acid dissociation constant of the cyanamide com-

plex, $(\text{NH}_3)_5\text{CoN}\equiv\text{C}-\text{NH}_2^{3+}$, was determined by potentiometric titration at 24.6, 34.8, and 43.8°. A weighed amount of $((\text{NH}_3)_5\text{CoN}\equiv\text{C}-\text{NH}_2)(\text{ClO}_4)_3$ was dissolved in 25.0 ml of 1.0M LiClO_4 and titrated with 0.010M NaOH in 1.0M LiClO_4 . The pK_a was determined from the pH at half neutralization since for the range of pH values involved this is a good approximation. The titration vessel was an all glass apparatus with hollow walls through which water was circulated in order to maintain a constant temperature. The pH measurements were made with a Beckman Expandomatic pH meter, calibrated at pH 4 and 7.

Instrumentation

All visible and ultraviolet spectra were recorded using a Cary Model 14 spectrophotometer. The proton magnetic resonance spectra were obtained using Varian A56/60 or Varian HA100 spectrometers.

All infrared measurements were made on a Perkin-Elmer 421 grating spectrophotometer, using potassium bromide disks and Nujol mulls.

The pH measurements were made on a Beckman Expandomatic pH meter.

CHARACTERIZATION OF COMPLEXES

Chapter III

Introduction

For a number of the complexes studied the possibility of linkage isomerism exists. For example both of the linkage isomers of formamide (NH_2CHO) have been prepared. For most of the other ligands studied, however, only one isomer was obtained. Before meaningful kinetic results can be obtained the bonding mode must be clearly established.

Most of the complexes studied were purified by cation exchange chromatography and the charge on the complex established qualitatively by the elution characteristics. In these cases the compounds separated as single bands on the ion exchange column and thus mixtures of similar complexes were readily separated. The complexes were all characterized by C, H, N analysis to confirm the stoichiometry but this does not differentiate between the possible linkage isomers. It has been found, however, that a combination of the visible absorption spectra, the infrared spectra, and the pmr spectra provide a strong indication of the isomer involved.

This section describes the various spectral measurements made on the complexes. The chemical characteristics of the compounds are also described and in some cases provide perhaps the most conclusive evidence for the assignment of the coordinating atom.

Visible and Ultraviolet Spectra.

The color and visible absorption spectra of the complexes provide a qualitative indication of the bonding differences between oxygen and nitrogen coordination. Oxygen bonded complexes are usually pink to red in color and have visible absorption spectra similar to the spectrum of $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ (λ_{max} at 345 nm and 492 nm). For nitrogen bonded complexes the solids are usually orange to yellow in color and have absorption spectra similar to $\text{Co}(\text{NH}_3)_6^{3+}$ (λ_{max} at 339 nm and 476 nm). This qualitative distinction also applies to the well-known nitro-nitritopentaammine-cobalt(III) complexes.

Table 1 summarizes the visible absorption behavior of the complexes studied. For the oxygen bonded compounds all the λ_{max} lie at lower energy than the parent aquo complex. This reflects the position in the spectrochemical series of a series of compounds for which OH_2 represents the simplest O-bonded ligand. In general this serves to qualitatively distinguish the O-bonded complexes from the nitrogen bonded compounds which usually lie higher in the spectrochemical series.

Several features of the visible absorption spectra of the nitrogen bonded compounds substantiate the nitrogen bonding formulation. First, the λ_{max} of $(\text{NH}_3)_5\text{CoNH}_2\text{CHO}^{3+}$ and $(\text{NH}_3)_5\text{CoNH}_2\text{C}(\text{O})\text{CH}_3^{3+}$ are almost identical to those of

Table 1

VISIBLE ABSORPTION SPECTRA OF PENTAAMMINECOBALT(III) COMPLEXES ^a

Bonding Mode	Complex	Visible Absorption Maxima, λ_{\max} (nm), (ϵ_{\max} (1 mole ⁻¹ cm ⁻¹))
Oxygen bonded	(NH ₃) ₅ CoOH ₂ ³⁺	345 (46.0) and 492 (49.0)
	(NH ₃) ₅ CoOCHNH ₂ ³⁺	346 (57.5) and 502 (68.8)
	(NH ₃) ₅ CoOCH(NHCH ₃) ³⁺	345 (66.6) and 504 (72.5)
	(NH ₃) ₅ CoOCHN(CH ₃) ₂ ³⁺	347 (66.7) and 506 (77.3)
	(NH ₃) ₅ CoOC(NH ₂) ₂ ³⁺	347 (54.2) and 514 (67.4)
	(NH ₃) ₅ CoOS(CH ₃) ₂ ³⁺	346 (56.9) and 517 (54.5)
	(NH ₃) ₅ CoO ₂ CNH ₂ ^{2+ b}	353 (61.8) and 505 (77.9)
	(NH ₃) ₅ CoO ₂ CNH ₂ ^{2+ c}	349 (51.8) and 507 (67.4)
	(NH ₃) ₅ CoO ₂ CC ₆ H ₄ CN ²⁺	349 (69.0) and 503 (82.0)
	(NH ₃) ₅ CoNH ₃ ³⁺	339 (45.8) and 476 (56.3)
Nitrogen bonded	(NH ₃) ₅ CoNHCHO ²⁺	348 (81.3) and 484 (68.4)
	(NH ₃) ₅ CoNHCHO ^{2+ d}	340 (58.2) and 478 (62.2)
	(NH ₃) ₅ CoNHC(O)CH ₃ ²⁺	351 (83.5) and 486 (71.1)
	(NH ₃) ₅ CoNHC(O)CH ₃ ^{2+ e}	341 (57.5) and 477 (61.5)

(continued)

Table 1 (continued)

Nitrogen bonded	$(\text{NH}_3)_5\text{CoNHC}(\text{O})\text{C}_6\text{H}_4\text{CN}^{2+}$	345 (117)	and	484 (83.2)
	$(\text{NH}_3)_5\text{CoNHC}(\text{O})\text{C}_6\text{H}_4\text{CN}^{2+}$ f	342 (87.6)	and	478 (73.5)
	$(\text{NH}_3)_5\text{CoNCNC}(\text{NH}_2)_2^{3+}$	348 (123)	and	487 (116)
	$(\text{NH}_3)_5\text{CoNCNH}_2^{3+}$ g	339 (65.3)	and	480 (73.7)
	$(\text{NH}_3)_5\text{CoNCNH}_2^{3+}$ h	304 (965)	and	521 (108)
	$(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{CN}^{3+}$	329 (86.5)	and	469 (78.5)
	$(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{OH}^{3+}$ i	---		472 (95.5)
	$(\text{NH}_3)_5\text{CoNCO}^{2+}$	353 (82.6)	and	501 (128)
	$(\text{NH}_3)_5\text{CoNCS}^{2+}$ j	306 (1486)	and	498 (179)

a All spectra in water unless otherwise noted.

b In 1.0M LiClO_4 and water.

c In 1.0M HClO_4 , as $(\text{NH}_3)_5\text{CoO}_2\text{CNH}_3^{3+}$

d In 1.0M HClO_4 as $(\text{NH}_3)_5\text{CoNH}_2\text{CHO}^{3+}$

e In 1.0M HClO_4 as $(\text{NH}_3)_5\text{CoNH}_2\text{C}(\text{O})\text{CH}_3^{3+}$

f In 1.0M HClO_4 as predominantly $(\text{NH}_3)_5\text{CoNH}_2\text{C}(\text{O})\text{C}_6\text{H}_4\text{CN}^{3+}$.

g In 1.0M HClO_4 .

(continued)

Footnotes to Table 1 (continued)

- h In 1.0M sodium acetate (pH 8.2) as $(\text{NH}_3)_5\text{CoN}=\text{C}=\text{NH}^{2+}$.
- i In 1.0M HClO_4 . The spectrum also shows a peak in the ultraviolet at 257 nm (ϵ , 2.16×10^4). In H_2O the maxima occur at 473 nm (ϵ , 108) and 295 nm (ϵ , 2.32×10^4).
- j D. A. Buckingham, I. I. Creaser, and A. M. Sargeson, Inorg. Chem., 9, 655 (1970).

$\text{Co}(\text{NH}_3)_6^{3+}$ as would be expected for coordination of a saturated nitrogen. Secondly, the large difference in the visible spectra of these complexes (see Figure 1(a) and (b)) on going from water to 1.0M HClO_4 would not be expected if the proton was being removed from a site remote from the $(\text{NH}_3)_5\text{Co}^{3+}$. The change observed for both the formamide and acetamide compounds is analogous to that found for the sulfamate³⁴ complex.

The cyanamide complex deserves special mention since a very large change in the visible spectrum shown in Figure 2 occurs on going from 1.0M HClO_4 to 1.0M sodium acetate. However in this case the proton is being removed from a remote (3 atoms removed) site. This large change is not anomalous since removal of a proton from the remote NH_2 group causes a substantial rearrangement of π electron density on going from $\text{N}\equiv\text{C}-\text{NH}_2$ to $(\text{N}=\text{C}=\text{NH})^-$. The conjugate base is isoelectronic with N_3^- , NCS^- , and NCO^- and it is not surprising that the spectrum of the cyanamide complex (conjugate base) is similar to the complexes of these ions. It should also be noted that molecular orbital calculations on cyanamide indicate that coordination through the nitrile group is favored over coordination through the amino group.³⁵

The spectra of the aromatic nitrile-coordinated complexes are very similar to that of $\text{Co}(\text{NH}_3)_6^{3+}$ with the λ_{max} at higher energy due to the influence of the nitrile group.

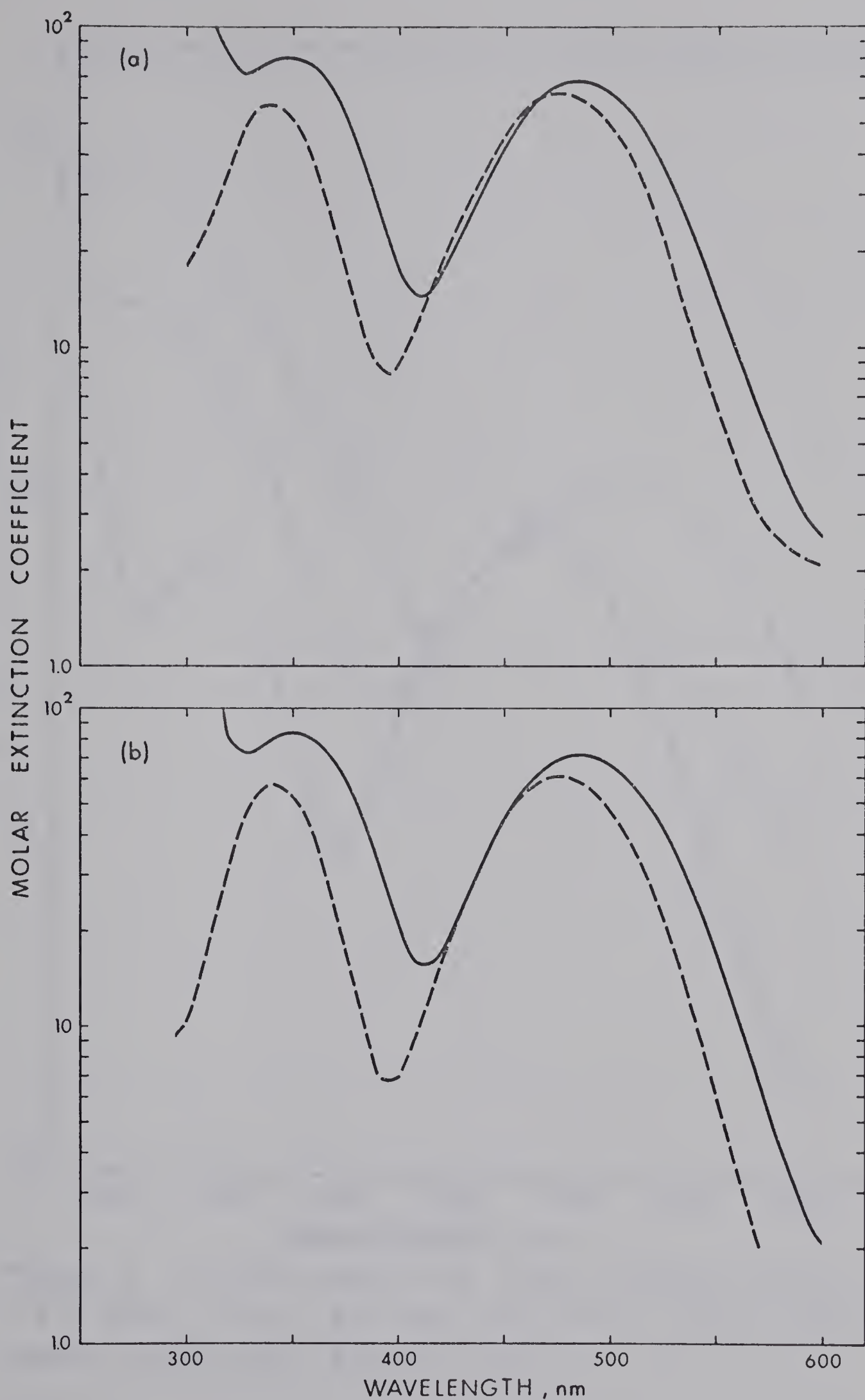


Figure 1. (a) Visible spectra of $((\text{NH}_3)_5\text{CoNHCHO})(\text{ClO}_4)_2$ in H_2O (—), and 1.0 M HClO_4 (----). (b) Visible spectra of $((\text{NH}_3)_5\text{CoNHC(O)ClO}_4)_2$ in H_2O (—), and 1.0 M HClO_4 (----).

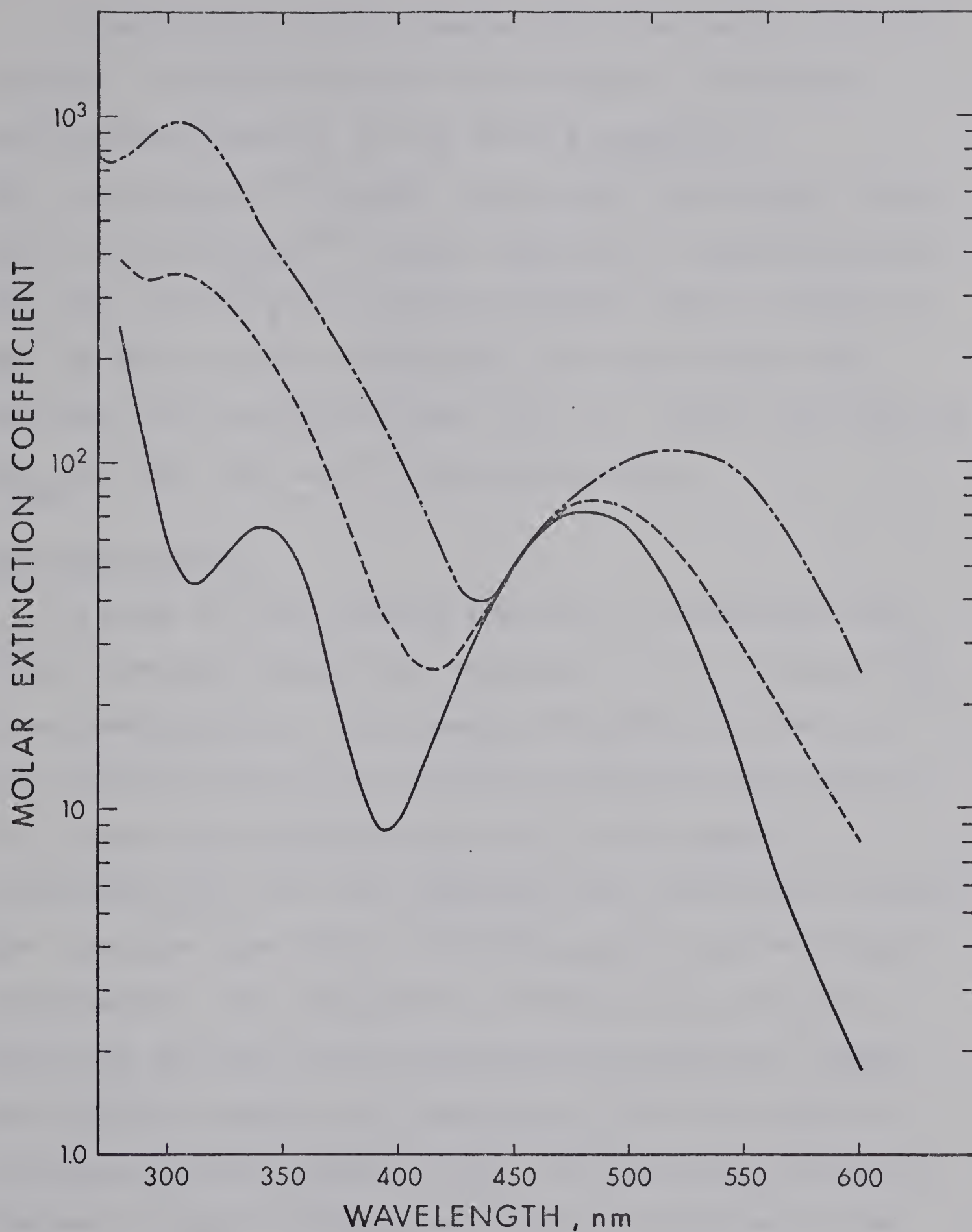


Figure 2. Visible spectra of $((\text{NH}_3)_5\text{CONCNH}_2)(\text{ClO}_4)_3$ in 1.0 M HClO_4 (—), H_2O (pH ~3.7) (----), and 1.0 M sodium acetate (pH ~8.2) (— · —).

A particularly good example for illustrating the differences in visible spectra due solely to a different coordinating function is the visible spectra of $(\text{NH}_3)_5\text{CoO}_2\text{CC}_6\text{H}_4\text{CN}^{2+}$ (bonded through the carboxylate oxygen), $(\text{NH}_3)_5\text{CoNHC(O)C}_6\text{H}_4\text{CN}^{2+}$ (bonded through the amide nitrogen), and $(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{CN}^{3+}$ (nitrile bonded) shown in figure 3. The low energy peaks confirm the spectrochemical order expected for coordination with nitrile > amide > carboxylate. (λ_{max} at 469, 484, and 503 nm respectively).

Infrared Spectra.

A study of the infrared spectra of coordination complexes sometimes allows the assignment of the coordinating atom unambiguously. For example, Penland and co-workers³⁶ have clearly shown by an analysis of the infrared spectra of a number of urea complexes that in the complex $\text{Pt}(\text{NH}_2\text{CONH}_2)_2\text{Cl}_2$ the urea molecules are coordinated through the nitrogen atom while $\text{Cu}(\text{OC}(\text{NH}_2)_2)_2\text{Cl}_2$ involves oxygen coordination. The assignment is based on the relative shifts of the C=O and C-N stretching frequencies. Oxygen coordination results in a decrease of the C=O stretching frequency and an increase in the C-N stretching frequency whereas nitrogen coordination causes an increase in the C=O stretching frequency and a decrease in the C-N stretching frequency. Similar attempts to assign the bonding atom in dimethylsulfoxide complexes using the shift of the S-O stretching frequency have not been as successful.^{37,38}

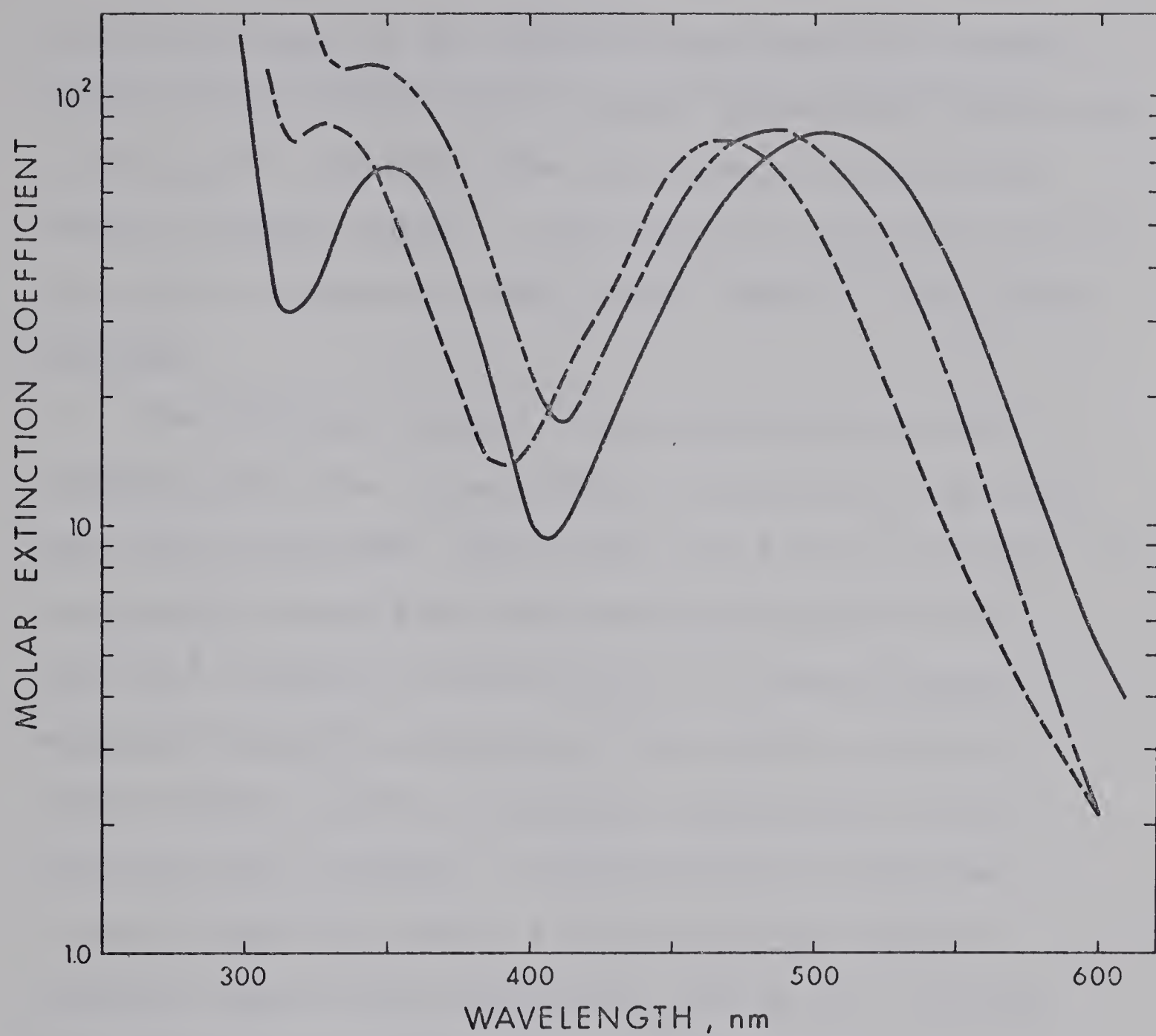


Figure 3. Visible spectra of $((\text{NH}_3)_5\text{CoO}_2\text{CC}_6\text{H}_4\text{CN})(\text{ClO}_4)_2$ (—), $((\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{CN})(\text{ClO}_4)_3$ (----), and $((\text{NH}_3)_5\text{CoNHCOC}_6\text{H}_4\text{CN})(\text{ClO}_4)_2$ (— · — · —) in H_2O .

As will be shown in the following section the interpretation of the shifts of the various stretching frequencies in $(\text{NH}_3)_5\text{Co}^{3+}$ complexes does not always differentiate between linkage isomers. Also, with the exception of the C=O and C \equiv N stretching modes, other modes are not easily assigned.

The infrared spectra of pentaamminecobalt(III) complexes show the characteristic vibrations of coordinated NH_3 in the 3000, 1600, 1315, and 830 cm^{-1} regions.³⁹ Deuteration causes the broad ammonia absorption at 1600 cm^{-1} to shift to about 1150 cm^{-1} permitting the carbonyl stretching frequency to be readily observed. Table 2 lists the C=O stretching frequencies for the bound and free ligands of the appropriate complexes. It can be seen from Table 2 that the oxygen bonded complexes show a low energy shift (25-50 cm^{-1}) of the C=O stretching frequency with respect to the free ligand. This is consistent with oxygen bonding but does not differentiate between possible linkage isomers since the same relative shifts are observed for the acidic form of the N isomers of formamide and acetamide.

The large differences in the carbonyl stretching modes of the acidic and basic forms of the N isomers of formamide and acetamide may be rationalized in terms of the π bonding in the N-C-O system. Such conjugation

Table 2

CARBONYL STRETCHING FREQUENCIES OF FREE AND COMPLEXED

<u>LIGAND</u> ^a		
C=O stretching frequency, cm ⁻¹		
Complex	Bound	Free
(NH ₃) ₅ CoNHCHO ²⁺	1600	1716 ^b
(NH ₃) ₅ CoNH ₂ CHO ³⁺	1675	1716 ^b
(NH ₃) ₅ CoOCHNH ₂ ³⁺	1675	1716 ^b
(NH ₃) ₅ CoOCH(NHCH ₃) ³⁺	1660	1666 ^c
(NH ₃) ₅ CoOCHN(CH ₃) ₂ ³⁺	1655	1681 ^d
(NH ₃) ₅ CoOC(NH ₂) ₂ ³⁺	1640 ^e	1686 ^c
(NH ₃) ₅ CoNHC(O)CH ₃ ²⁺	1560	1714 ^c
(NH ₃) ₅ CoNH ₂ C(O)CH ₃ ³⁺	1700	1714 ^c
(NH ₃) ₅ CoO ₂ CNH ₂ ²⁺	1560	1725 ^f
(NH ₃) ₅ CoO ₂ CC ₆ H ₄ CN ²⁺	1600	1700 ^g

^a Spectra of the deuterated form of the complex in KBr disks and Nujol mulls show the same C=O stretching frequency.

^b R. G. Puranik and K. Venkata Ramiah, J. Mol. Spectrosc., 3, 486 (1969).

^c L. J. Bellamy in "Advances in Infrared Group Frequencies," Methuen and Co., Great Britain, 1968, p 155.

^d J. Archambault and R. Rivest, Can. J. Chem., 38, 1331 (1960).

^e C-N stretching frequency at 1490 cm⁻¹.

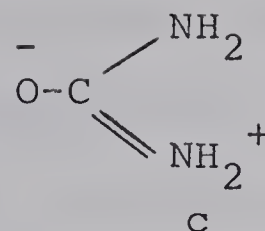
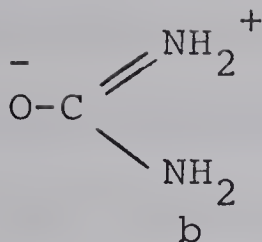
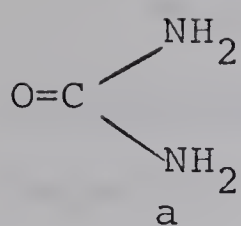
^f C=O stretching frequency for urethane from reference c.

^g This work.

is possible in the basic form of the N isomers and electron withdrawal from the N atom is at least partially compensated for by delocalization from the C=O bond, with a resulting decrease in the C=O stretching frequency. In the acidic form all orbitals on the nitrogen are used in σ bonding and the nitrogen is no longer in conjugation with the C=O system. Therefore the C=O stretch is much less affected by the $(\text{NH}_3)_5\text{Co}^{3+}$.

For the oxygen bonded complexes of formamide, N-methylformamide, and N,N-dimethylformamide, electron withdrawal from the C=O bond can be compensated for by electron donation from NH_2 , $\text{NH}(\text{CH}_3)$, and $\text{N}(\text{CH}_3)_2$ through the N-C π bond, with a resultant smaller decrease in the C=O stretching frequency.

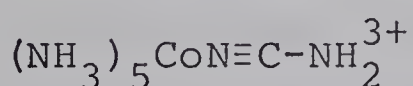
For the urea complex the bands at 1640 and 1590 cm^{-1} can be assigned to the $\nu(\text{C=O})$ and NH_2 bending vibrations respectively. The absorption band at 1490 cm^{-1} , which shows no isotopic shift on deuteration, can be attributed to the CN skeletal vibration. For free urea the $\nu(\text{C=O})$, NH_2 bending, and C-N vibrations occur at 1683, 1603, and 1471 cm^{-1} respectively.⁴⁰ Complexation has resulted in a decrease in the C=O stretching frequency and an increase in the CN stretching frequency. If urea may be represented by resonance hybrids a, b, and c then coordination through oxygen favours b and c



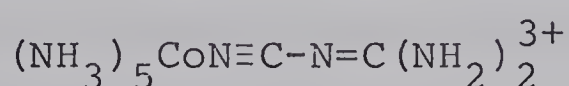
over a, thus decreasing the double bond character of the CO group. This results in the decreased C=O stretching frequency. Similarly $\nu(\text{C-N})$ should be increased due to contributions from b and c. Therefore on the above basis the complex may be formulated as bonding through the carbonyl oxygen.

For the dimethylsulfoxide complex the infrared spectrum shows a strong band at 945 cm^{-1} and a peak of medium intensity at 985 cm^{-1} . Bands at ~ 980 and 950 cm^{-1} have also been observed for a number of transition metal complexes of DMSO for Mn(II), Co(II), Ni(II) and Cu(II).^{37,38,41} There is some question as to the assignment of the S-O stretch in this region and Drago and Meek³⁸ have assigned the band at $\sim 980\text{ cm}^{-1}$ to the S-O stretch and the band at $\sim 950\text{ cm}^{-1}$ to the CH_3 rocking vibrations whereas Cotton and coworkers³⁷ have reversed the assignments. However the band near 950 cm^{-1} does not occur in the complexes of diphenylsulfoxide⁴¹ and, on this basis, the band near 980 cm^{-1} can be assigned to the S-O stretching vibration. Since the S-O stretch in free DMSO occurs at 1045 cm^{-1} the pentaamminecobalt(III) DMSO complex is assumed to be coordinated through the oxygen using similar arguments as in the urea case.

The characteristic $C\equiv N$ stretching frequencies of the nitrile complexes are given in Table 3 along with the corresponding frequencies for the free ligands. In all cases the $C\equiv N$ stretching frequency increases upon coordination. This behavior is also observed for nitrile complexes of $(NH_3)_5Ru^{3+}$.⁴² For the terephthalonitrile and 4-cyanobenzoate complexes the $C\equiv N$ stretching frequency for the uncoordinated nitrile is little affected by complexation. Thus the 4-cyanophenol complex must be bonded through the nitrile since there is a 45 cm^{-1} shift to higher wavelength with respect to the free ligand. Also, the changes in stretching frequency provide the first indication that the cyanamide and N-cyanoguanidine are bonded to cobalt through the nitrile group as shown in structures XIII and XIV, and not through the amino group.



XIII

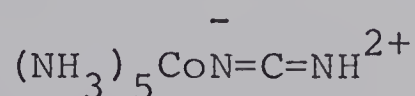
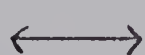


XIV

The $C\equiv N$ stretch in the conjugate base of the cyanamide complex occurs at 2150 cm^{-1} , shifted to lower frequency, as expected if resonance form XV (b) makes a significant contribution in the conjugate base.



XV (a)



XV (b)

Table 3STRETCHING FREQUENCIES, $\nu(\text{C}\equiv\text{N})$ FOR NITRILES

Ligand	Stretching Frequency ^a , cm^{-1}		Ref.
	Complexed	Free Ligand	
N-cyanoguanidine	2200, 2260 (s)	2115, 2165 (s), 2210	this work
Cyanamide ^b	2310	2210-2250	this work
1,4-dicyanobenzene	2235, ^c 2290	2230	this work
4-cyanophenyl	2280	2235	this work
Acetonitrile	2320	2267 ^d	e

^a Identical results were obtained using KBr disks or Nujol mulls.

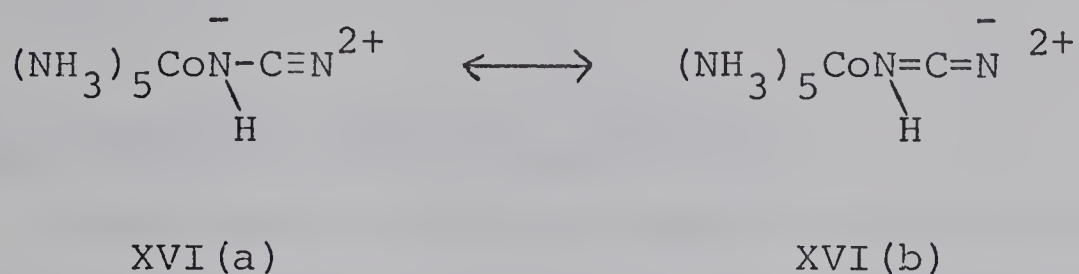
^b The conjugate base has $\nu(\text{C}\equiv\text{N})$ at 2150 cm^{-1} .

^c This is assigned to the uncoordinated $\text{C}\equiv\text{N}$ from comparison to the free ligand.

^d L. J. Bellamy, "Advances in Infrared Group Frequencies", Methuen & Co., Great Britain, 1968, p 68.

^e R. B. Jordan, A. M. Sargeson and H. Taube, Inorg. Chem., 5, 1091 (1966).

If cyanamide were bonded through the NH_2 then resonance structures XVI(a) and XVI(b) can be drawn for the conjugate base. However XVI(b) would not be favored because



it involves movement of electron density away from the cobalt(III) atom. Therefore a relatively small change in the $\text{C}\equiv\text{N}$ stretching frequency would be expected for bonding through the amino group whereas the shift is large (160 cm^{-1}).

Tautomerism between XV and XVI is also possible but XV must be favored to account for the frequency shift on formation of the conjugate base.

The infrared spectrum of the isocyanato complex has $\nu_1(\text{C-O})$ and $\nu_3(\text{C-N})$ at 1335 and 2265 cm^{-1} respectively. Both the C-O and C-N stretching bands appear at higher frequencies than those in an ionic cyanate (for KNCO , $\nu_1(\text{C-O})$ and $\nu_3(\text{C-N})$ are at 1254 and 2158 cm^{-1}) and are consistent with those of other known N-bonded cyanate complexes.⁴³

The infrared spectrum of $(\text{NH}_3)_5\text{CoNHCHOCO}(\text{NH}_3)_5^{5+}$ is of no particular diagnostic value except for the presence of a strong absorption at 1601 cm^{-1} in the

deuterated complex. This band can be attributed to the C=O stretching frequency. It is interesting to note that the C=O stretching frequency for $(\text{NH}_3)_5\text{CoNHCHO}^{2+}$ appears at 1600 cm^{-1} .

Proton Magnetic Resonance Spectra

The observed chemical shifts for the complexes studied are given in Table 4. Also included in Table 4 are the chemical shifts of known oxygen and nitrogen bonded complexes for comparison.

It has been found that the chemical shift difference between the cis and trans NH_3 protons is $1.0 - 1.5\ \tau$ for an O-bonded ligand and $0 - 0.6\ \tau$ for an N-bonded ligand. The results in Table 4 conform to this empirical rule. The relative shifts of the cis and trans NH_3 protons have been discussed in a more theoretical manner by Hendrickson and Jolly.⁴⁴

The pmr spectra are also useful in confirming the presence of all the chemical groups in the ligand. Figure 4 shows the pmr spectra of the oxygen bonded complexes of formamide, N-methylformamide, and N,N-dimethylformamide. For these complexes the assignments are quite easily made by a comparison to the free ligands and other O-bonded complexes. For the N-methylformamide complex spin-decoupling experiments have shown that the C-H and N-H protons are coupled with a coupling constant (J) of $\sim 3\text{ Hz}$ and also that the N-H and CH_3 protons are

Table 4

PMR DATA FOR PENTAAMMINECOBALT(III) COMPLEXES IN DEUTERATED
DIMETHYLSULFOXIDE ^a.

<u>Complex</u> ^b	<u>cis-NH₃</u>	<u>trans-NH₃</u>	<u>Others</u>
$(\text{NH}_3)_5\text{CoNH}_3^{3+}$	-	6.78	-
$(\text{NH}_3)_5\text{CoOH}_2^{3+}$	6.22	7.25	OH_2 4.30
$(\text{NH}_3)_5\text{CoOCHNH}_2^{3+}$	6.16	7.26	CH 2.62; NH_2 6.16
$(\text{NH}_3)_5\text{CoOCH}(\text{NHCH}_3)^{3+}$	6.13	7.26	CH^c 2.52, 2.56 doublet CH_3^c 7.22, 7.28 doublet NH 0.20
$(\text{NH}_3)_5\text{CoOCHN}(\text{CH}_3)_2^{3+}$	6.14	7.28	CH 2.60; $\text{N}(\text{CH}_3)_2$ 6.92, 7.10
$(\text{NH}_3)_5\text{CoOC}(\text{NH}_2)_2^{3+}$	6.10	7.48	$(\text{NH}_2)_2$ 3.37
$(\text{NH}_3)_5\text{CoOS}(\text{CH}_3)_2^{3+}$	6.13	7.48	$(\text{CH}_3)_2$ 7.24
$(\text{NH}_3)_5\text{CoO}_2\text{CH}^{2+}$	6.32	7.34	CH 2.54
$(\text{NH}_3)_5\text{CoO}_2\text{CNH}_2^{2+}$	6.24	7.42	NH_2 4.79
$(\text{NH}_3)_5\text{CoO}_2\text{CCH}_3^{2+}$	6.31	7.36	CH_3 8.18
$(\text{NH}_3)_5\text{CoO}_2\text{CCH}_2\text{Cl}^{2+}$	6.26	7.35	CH_2 6.02
$(\text{NH}_3)_5\text{CoO}_2\text{CCHCl}_2^{2+}$	6.22	7.31	CH 3.87
$(\text{NH}_3)_5\text{CoO}_2\text{CCCl}_3^{2+}$	6.14	7.22	
$(\text{NH}_3)_5\text{CoO}_2\text{CCF}_3^{2+}$	6.14	7.31	
$(\text{NH}_3)_5\text{CoO}_2\text{C}_6\text{H}_5^{2+}$	6.15	7.27	ring protons- multiplet cen- tered at 2.10 and 2.60
$(\text{NH}_3)_5\text{CoO}_2\text{CC}_6\text{H}_4\text{CN}^{2+}$	6.14	7.26	ring protons 1.89, 2.02, 2.11, 2.24.

Table 4 (continued)

$(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{OH}^{3+}$	6.17	6.59	OH -0.54; ring protons 2.09, 2.24, 2.87, 3.01.
$(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{O}_2\text{CCH}_3^{3+}$	6.14	6.58	CH_3 7.67; ring protons 1.86, 1.99, 2.38, 2.53.
$(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{CN}^{3+}$	6.12	6.54	ring protons, singlet at 1.78.
$(\text{NH}_3)_5\text{CoNHCOC}_6\text{H}_4\text{CN}^{2+}$	6.63	6.78	ring protons, singlet at 2.02 NH 5.14.
$(\text{NH}_3)_5\text{CoNCNH}_2^{3+}$	6.33	6.83	NH $_2$ 1.87.
$(\text{NH}_3)_5\text{CoNCNC(O)CH}_3^{2+}$ d	6.34	6.84	CH_3 8.09.
$(\text{NH}_3)_5\text{CoNCNC(NH}_2)_2^{3+}$	6.18	6.62	(NH $_2$) $_2$ 2.68.
$(\text{NH}_3)_5\text{CoNHCHO}^{2+}$	6.78	6.78	CH e 1.96; NH f 6.14.
$(\text{NH}_3)_5\text{CoNH}_2\text{CHO}^{2+}$ g	6.68	6.68	CH 2.66; NH $_2$ 6.18.
$(\text{NH}_3)_5\text{CoNHC(O)CH}_3^{2+}$	6.77	6.77	CH 8.03; NH 6.27
$(\text{NH}_3)_5\text{CoNH}_2\text{C(O)CH}_3^{3+}$	6.70	6.70	CH_3 7.76; NH $_2$ 6.09
$(\text{NH}_3)_5\text{CoNH}\text{SO}_3^+$	6.47	6.77	NH 5.48
$(\text{NH}_3)_5\text{CoNH}_2\text{SO}_3^{2+}$	6.47	6.77	NH $_2$ 3.46
$(\text{NH}_3)_5\text{CoNCO}^{2+}$	6.58	7.08	
$(\text{NH}_3)_5\text{CoN}_3^{2+}$	6.68	7.00	
$(\text{NH}_3)_5\text{CoCN}^{2+}$	7.13	6.25	
$(\text{NH}_3)_5\text{CoCl}^{2+}$	6.43	7.11	

continued

- a All values are in τ with respect to the solvent peak at 7.48 τ .
- b Complexes were all perchlorate salts.
- c Spin decoupling experiments have shown that the C-H proton is coupled to the NH proton with $J \sim 3$ Hz, and the NH proton is also coupled to the CH_3 protons with $J = 5$ Hz.
- d For $(\text{NH}_3)_5\text{CONCNHC}(\text{O})\text{CH}_3^{3+}$ the proton exchanged with H_2O in the solvent.
- e Doublet due to coupling with formamide NH proton, $J = 3.8$ Hz.
- f Assignment confirmed by spin decoupling of CH resonance.
- g Spectrum obtained by adding TFA to d_6 -DMSO.

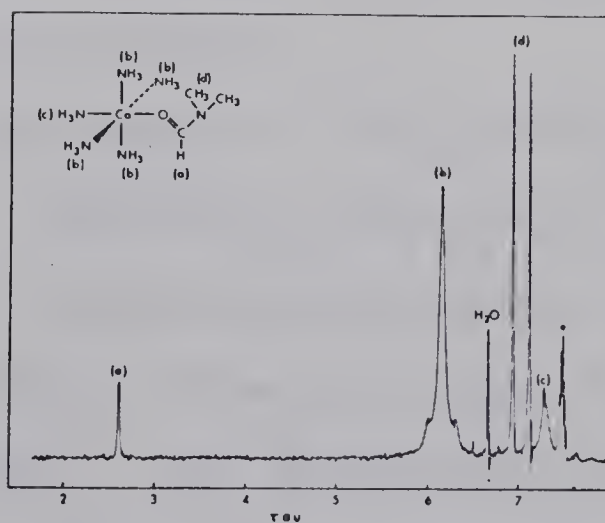
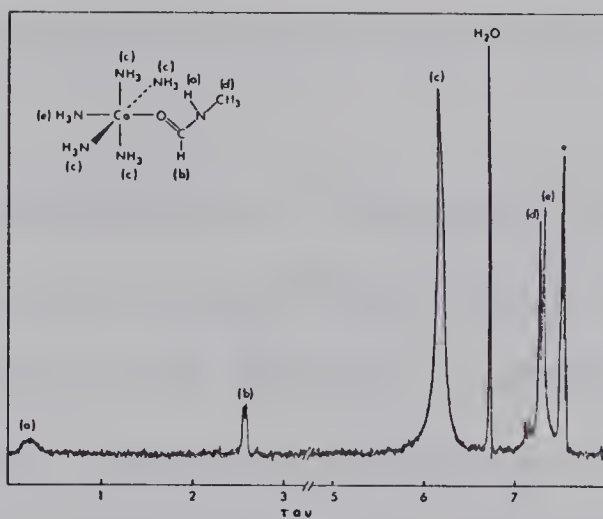
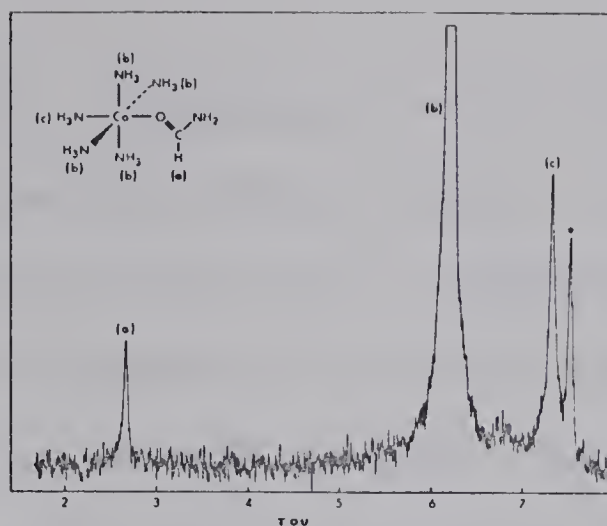


Figure 4. Pmr spectra in d_6 -dimethylsulfoxide of the oxygen bonded pentaamminecobalt(III) complexes of formamide, N-methylformamide, and dimethylformamide (all at 100 MHz.).

coupled with $J = 5$ Hz. Irradiation of the C-H proton produced no change in the CH_3 doublet and it is concluded that coupling between C-H and CH_3 is negligible. In the case of the formamide complex no coupling between C-H and NH_2 was observed. For the DMF complex a temperature study was undertaken to try to observe averaging of the two methyl resonances. In this case solvolysis to give the DMSO complex and free DMF occurred at about 55° and no merging of the CH_3 resonances was observed below this temperature.

In Figure 5 the spectra of $(\text{NH}_3)_5\text{CoNHCHO}^{2+}$, $(\text{NH}_3)_5\text{CoNHC(O)CH}_3^{2+}$, and $(\text{NH}_3)_5\text{CoNH}_2\text{C(O)CH}_3^{3+}$ are shown. Again the assignments can be made by a comparison to the free ligands. It seems somewhat surprising, however, that the CH_3 shift in the acidic form of the acetamide complex is quite different from the corresponding shift in the basic form, since the NH_2 and NH resonances do not shift by an appreciable amount.

In Figure 6 the spectra of $(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{CN}^{3+}$, $(\text{NH}_3)_5\text{CoNHCOC}_6\text{H}_4\text{CN}^{2+}$, and $(\text{NH}_3)_5\text{CoO}_2\text{CC}_6\text{H}_4\text{CN}^{2+}$ are shown. The spectrum of the 4-cyanobenzoate complex is typical of the oxygen bonded ligands showing the cis NH_3 at 6.14 τ and trans NH_3 at 7.26 τ . The aromatic protons show a multiplet centred at 2.06 τ . In sharp contrast to this, the ring protons in the terephthalonitrile complex resonate as a singlet at 1.78 τ while the cis and trans NH_3 appear

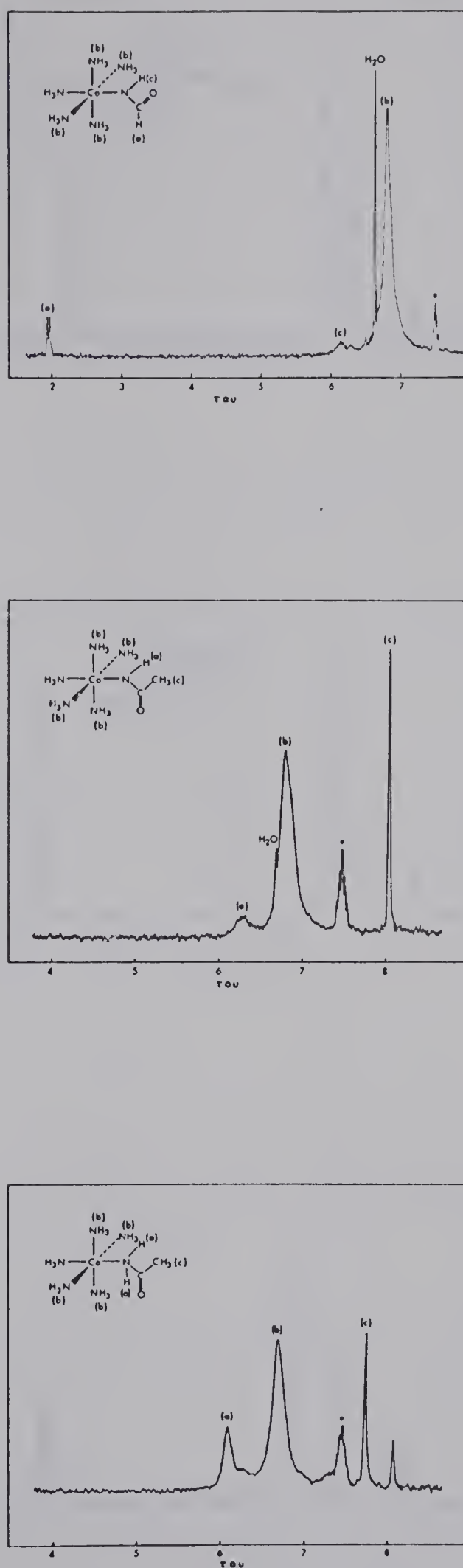


Figure 5. Pmr spectra in d_6 -dimethylsulfoxide of $(\text{NH}_3)_5\text{CoNHCHO}^{2+}$ (at 100 MHz), $(\text{NH}_3)_5\text{CoNHCH(O)CH}_3^{2+}$, and $(\text{NH}_3)_5\text{CoNH}_2\text{C(O)CH}_3^{3+}$ (at 60 MHz).

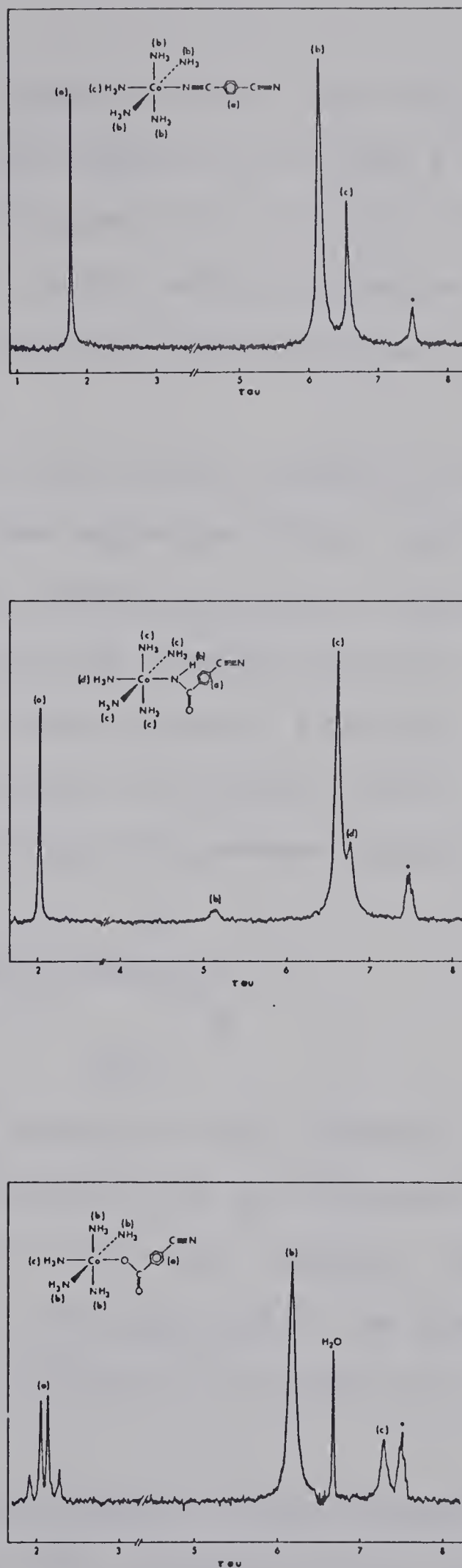


Figure 6. PMR spectra in d_6 -dimethylsulfoxide of $(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{CN}^{3+}$ (at 100 MHz), $(\text{NH}_3)_5\text{NHCOC}_6\text{H}_4\text{CN}^{2+}$ (at 60 MHz), and $(\text{NH}_3)_5\text{CoO}_2\text{CC}_6\text{H}_4\text{CN}^{2+}$ (at 60 MHz).

at 6.12 and 6.54 τ respectively. For $(\text{NH}_3)_5\text{CoNHCOC}_6\text{H}_4\text{CN}^{2+}$ the cis and trans NH_3 appear at 6.63 and 6.78 τ and again the aromatic protons appear as a singlet at 2.02 τ . The appearance of this singlet was not expected when compared to the multiplet found for the structurally similar carboxylate compound.

The fact that all the NH_2 protons in the N-cyano-guanidine complex are equivalent shows that the ligand is bonded through the nitrile nitrogen. However, for the cyanamide complex the pmr spectrum does not help in differentiating the linkage isomers, although it does eliminate XVII since two different N-H protons, with a 1:12 integration relative to the cis NH_3 protons would be observed.

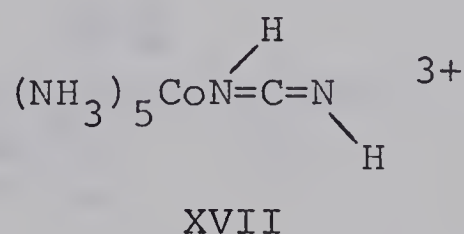


Figure 7 shows the spectra of the cyanamide complex along with the product obtained when the cyanamide complex is acylated (discussed in the next section). The presence of the CH_3 resonance in the spectrum of the reaction product confirms that the acylation did indeed take place as expected.

In Figure 8 the spectra of the 4-cyanophenol complex and the product from the reaction of the complex with acetic anhydride are shown. Again the spectrum of the acylation

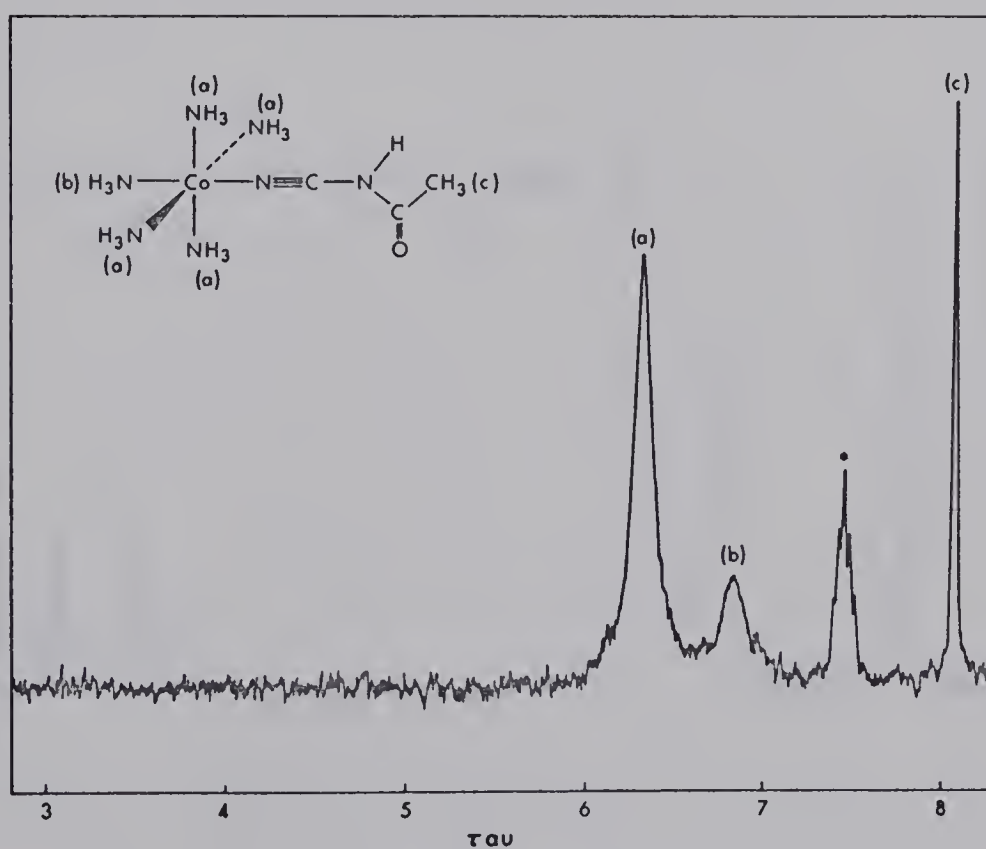
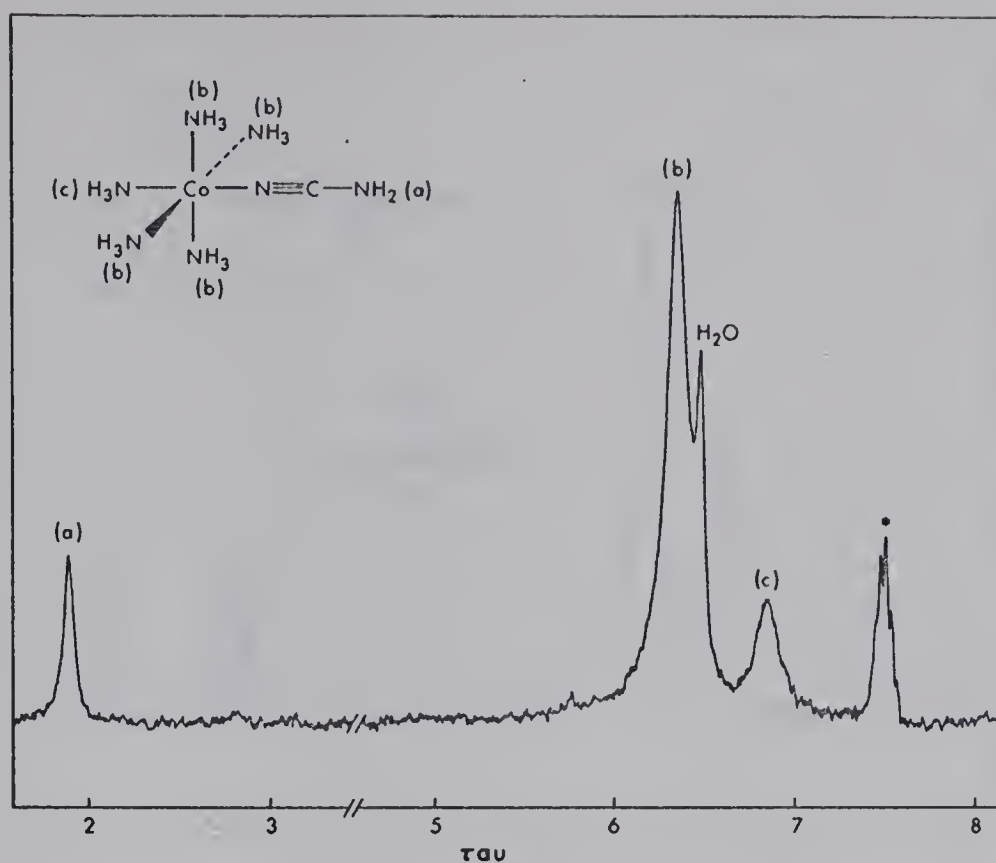


Figure 7. Pmr spectra in d_6 -dimethylsulfoxide of $(\text{NH}_3)_5\text{CoNCNH}_2^{3+}$ and $(\text{NH}_3)_5\text{CoNCNHC(O)CH}_3^{3+}$ (both at 60 MHz).

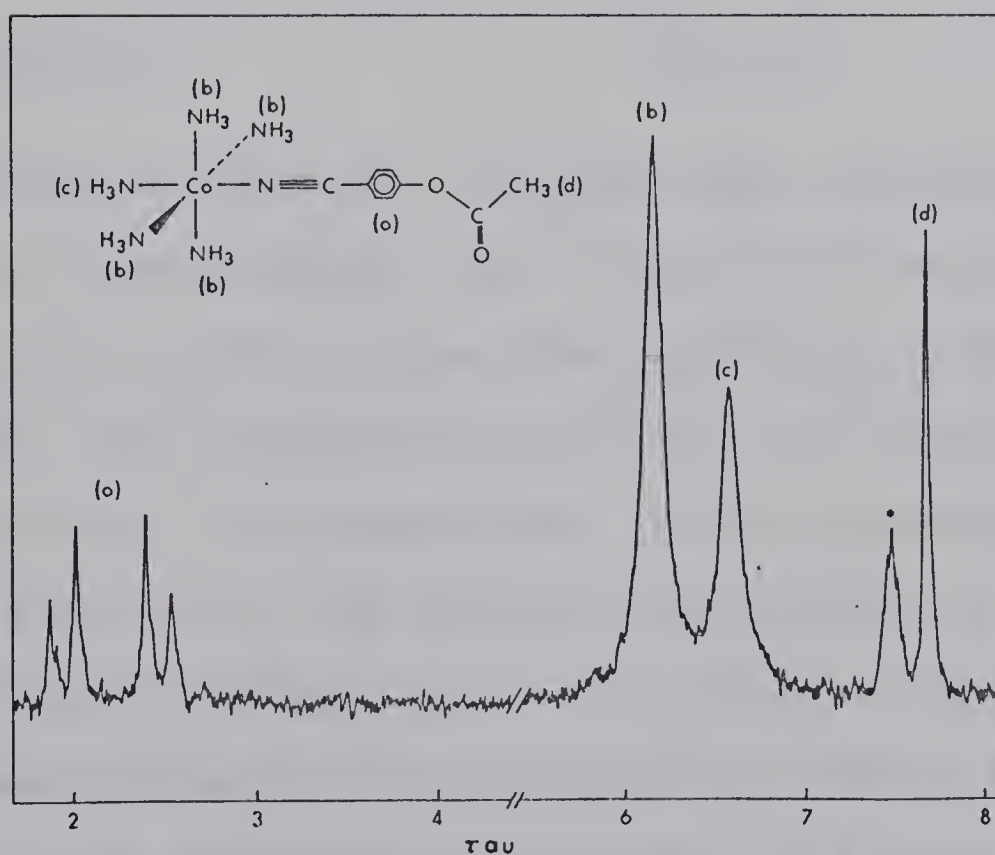
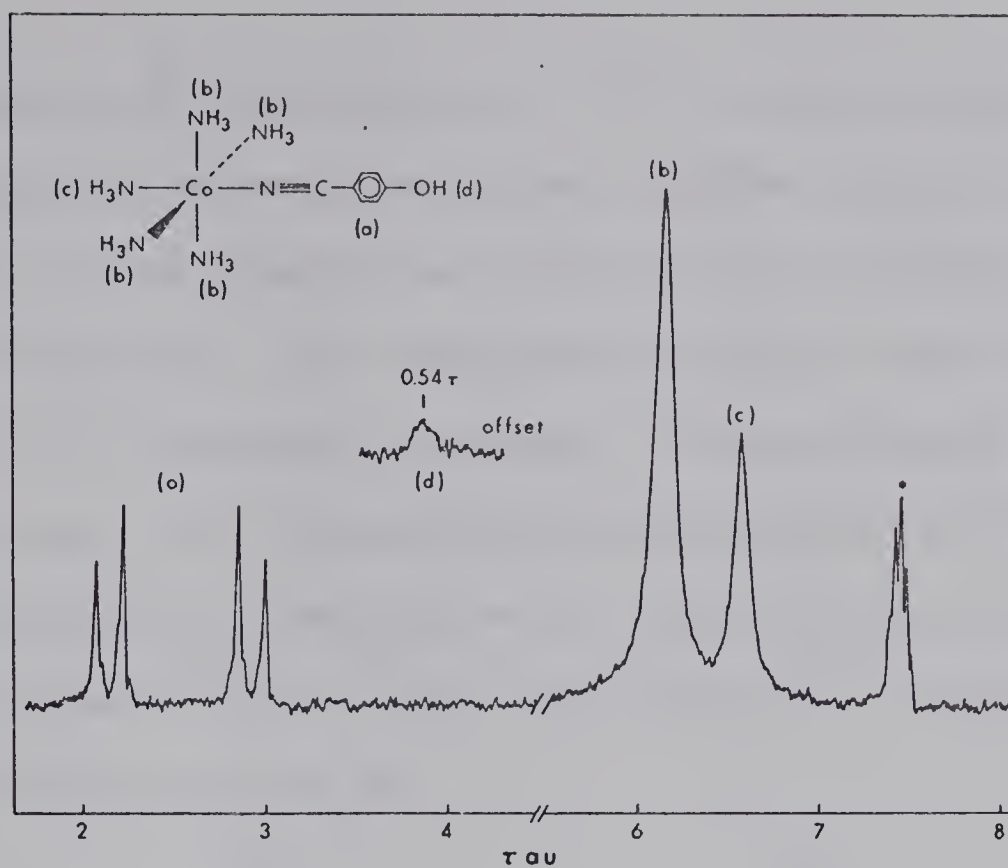
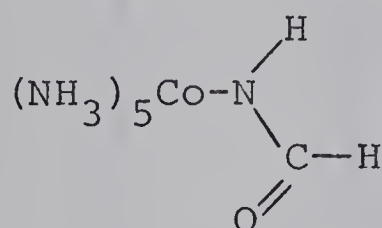


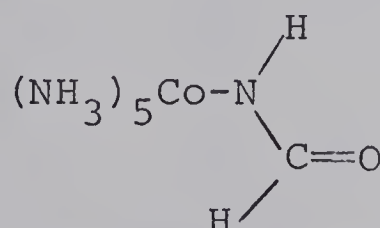
Figure 8. Pmr spectra in d_6 -dimethylsulfoxide of $(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{OH}^{3+}$ and $(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{O}_2\text{CCH}_3^{3+}$ (both at 60 MHz).

product shows a CH_3 resonance at 7.67 τ and confirms the product expected as well as giving further support to formulation of the complex as being nitrile bonded.

In a number of the complexes studied there is a possibility of rotational isomers. The conjugate base of the N isomer of formamidopentaamminecobalt(III) may be expected to show two resonances for the C-H proton due to rotational isomerization about the N-C bond, as shown in structures XVIII(a) and (b).



XVIII(a)



XVIII(b)

A low temperature pmr study in d_7 -DMF has confirmed the existence of these isomers. The changes in the spectrum with temperature indicate that one rotational isomer predominates at high temperature, but the two are present in equilibrium at low temperature. As the temperature is lowered, a peak due to the second isomer begins to appear downfield from the other peak. The relative intensity of the new peak increases, and its position shifts further downfield as the temperature decreases. A limiting spectrum cannot be obtained in DMF and therefore a quantitative analysis of the spectra in Figure 9 is not possible.

Restricted rotation has also been observed for the

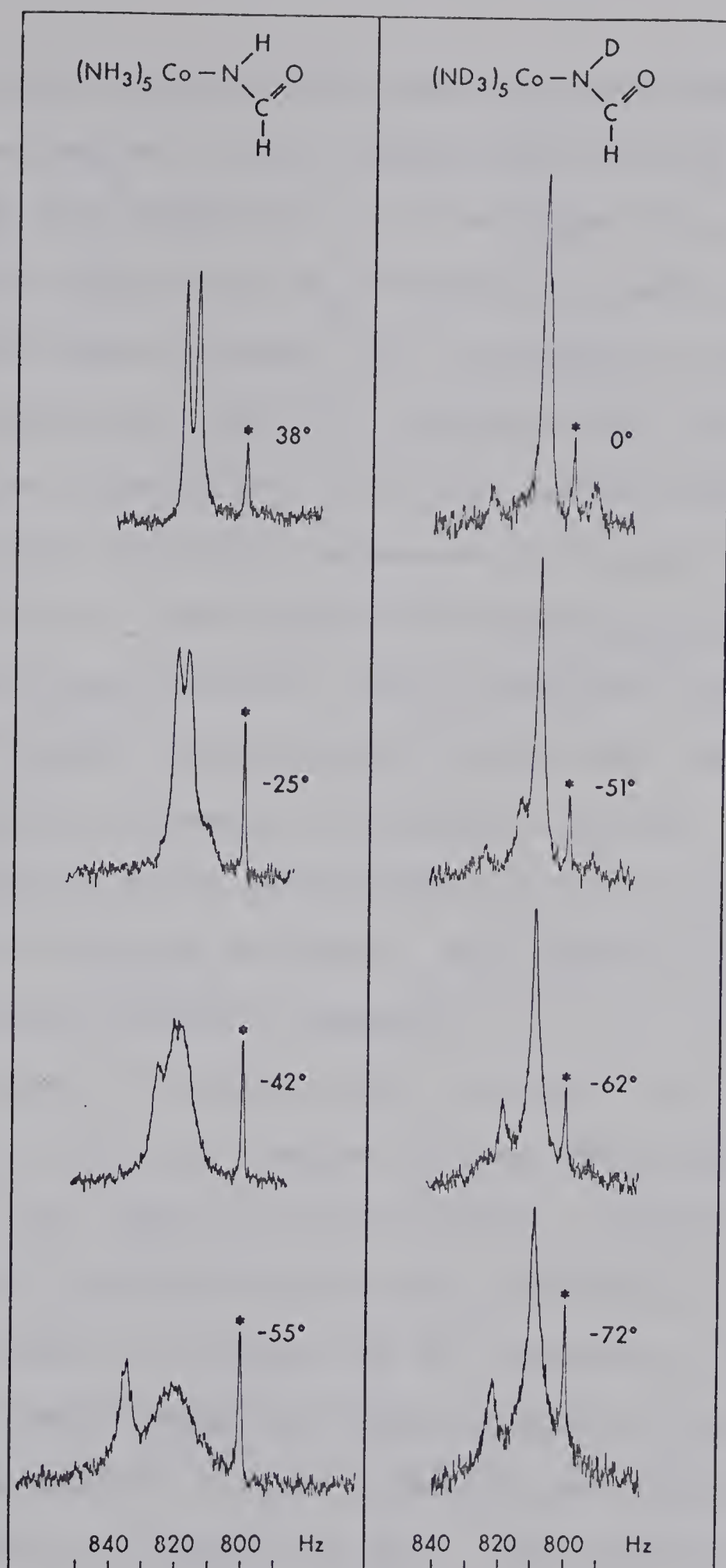


Figure 9. Temperature variation of the C-H pmr, in d_7 -DMF, of $(\text{NH}_3)_5 \text{CoNHCHO}^{2+}$ and $(\text{NH}_3)_5 \text{CoNDCHO}^{2+}$. An asterisk denotes solvent peak due to formyl C-H in DMF. Spectra recorded at 100 MHz.

carbamatopentaamminecobalt(III) and the urea complex. For the carbamate complex a sharp singlet is observed for the NH_2 resonance (see Figure 10) at room temperature. As the temperature is lowered the NH_2 resonance broadens and is split into two peaks at about -20° (100 MHz in d_7 -DMF). At 60 MHz the coalescence point is approximately -35° in d_7 -DMF. As the temperature is further lowered the peaks separate into two distinct resonances of unequal intensity.

An analysis of the spectra is complicated by the fact that both restricted O-C and/or C- NH_2 bond rotation can occur. This factor could account for the fact that the NH_2 peak splits into resonances of unequal intensity. It is hoped that some of these difficulties will be cleared up by a complete lineshape analysis. The chemical shift-intensity data are given in Appendix C.

The presence of only one NH_2 resonance at 3.37 τ in the spectrum of the urea complex at room temperature further confirms that the urea is oxygen bonded. Figure 11 shows the temperature variation of this NH_2 resonance in d_7 -DMF. As the temperature is lowered the NH_2 resonance is broadened and eventually separates into a doublet at -40° . Two distinct resonances of \sim equal intensity are obtained when the temperature is lowered to -60° . The spectra can be interpreted with reference to XIX by assuming only C- NH_2 restricted rotation since models indicate that O-C rotation

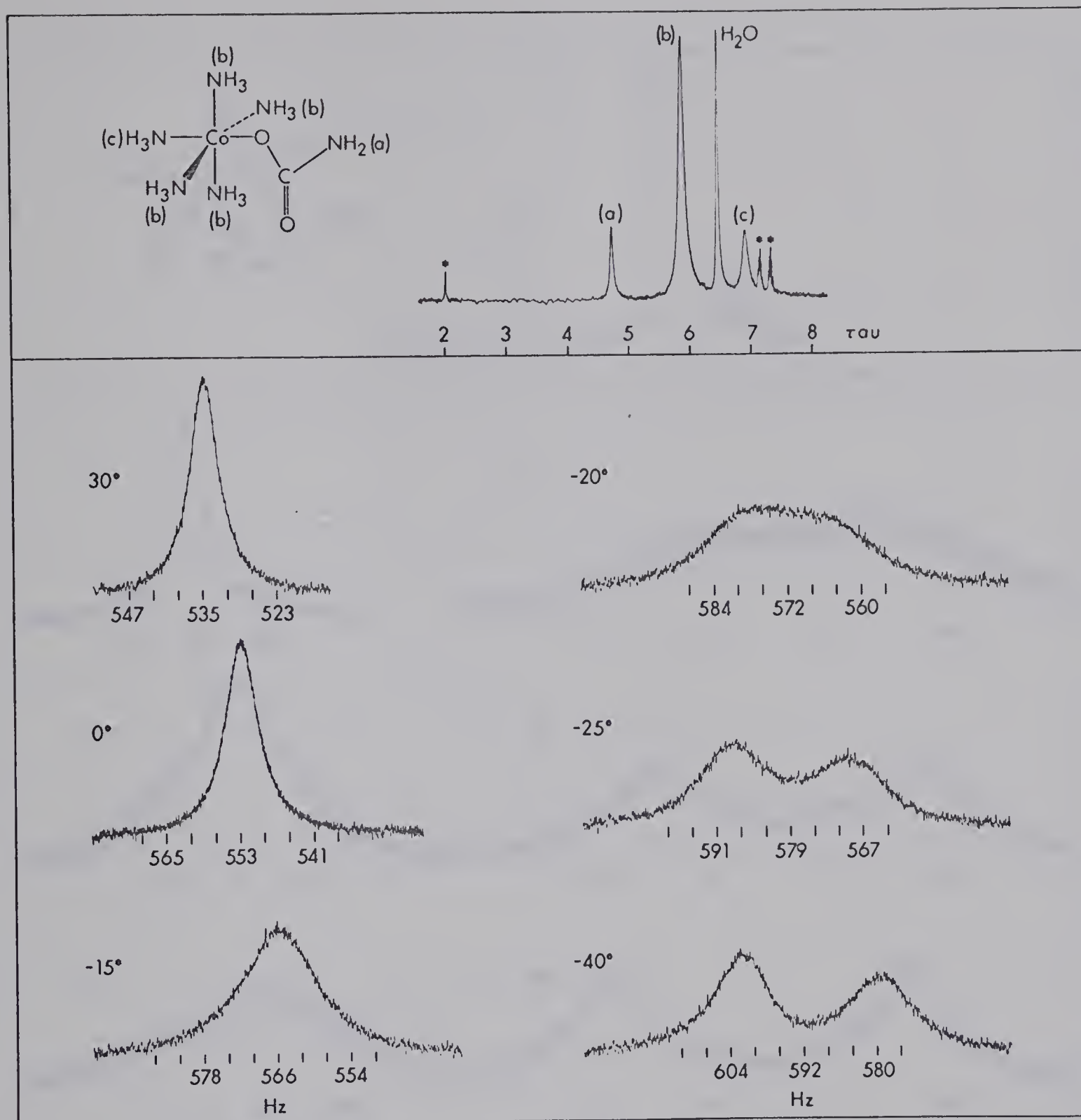


Figure 10. Temperature variation of the $\text{C}-\text{NH}_2$ pmr, in d_7 -DMF, of $(\text{NH}_3)_5\text{CoO}_2\text{CNH}_2^{2+}$. Spectra recorded at 100 MHz.

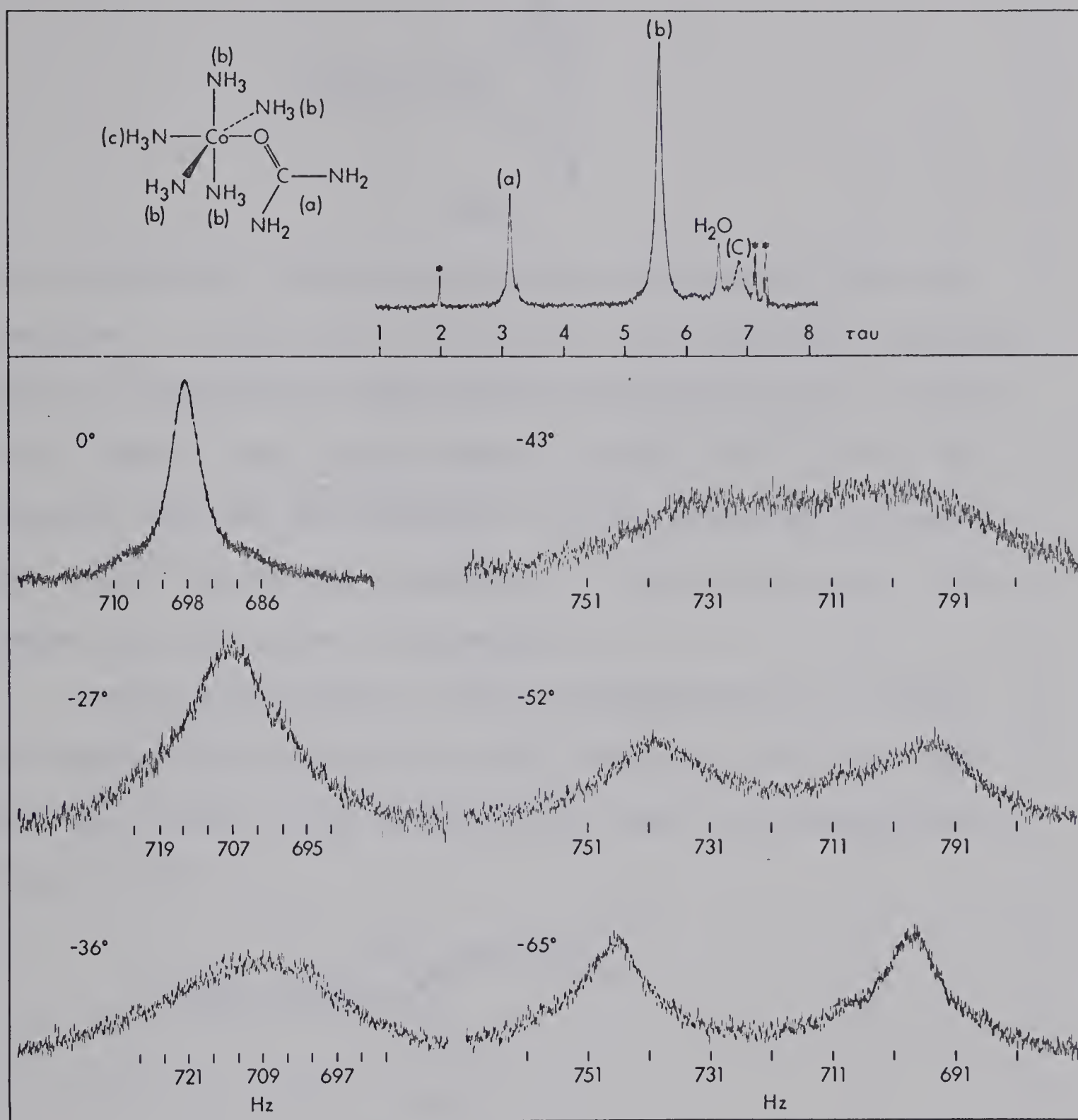
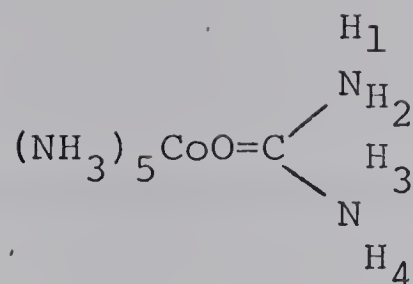


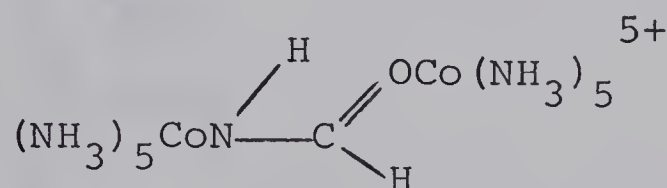
Figure 11. Temperature variation of the $\text{C}(\text{NH}_2)_2$ pmr, in d_7 -DMF, of $(\text{NH}_3)_5\text{CoOC}(\text{NH}_2)_2^{3+}$. Spectra recorded at 100 MHz.



XIX

is not possible without distortion and loss of C-N conjugation. On the basis of XIX two well separated doublets would be expected in the frozen configuration due to protons 2 and 3, and 1 and 4 where 1 and 2, and 3 and 4 are coupled. However the doublets are not observed presumably due to N^{14} quadrupole relaxation. The experimental line-shape data are given in Appendix D.

The pmr spectrum of $(\text{NH}_3)_5\text{CoNHCHOCO}(\text{NH}_3)_5^{5+}$ shown in Figure 12 provides the first indication that the complex is a dimer. The spectrum can best be interpreted in terms of XX



XX

The resonances at 6.37 and 6.94 τ can be assigned to the four cis NH_3 ligands of each Co(III) unit, and the resonances for the trans NH_3 of each Co(III) unit at 6.73 and 7.26 τ respectively. The C-H proton resonance appears at 2.78 τ while the N-H appears at 3.96 τ . In addition, these protons have been shown to be coupled, by double resonance

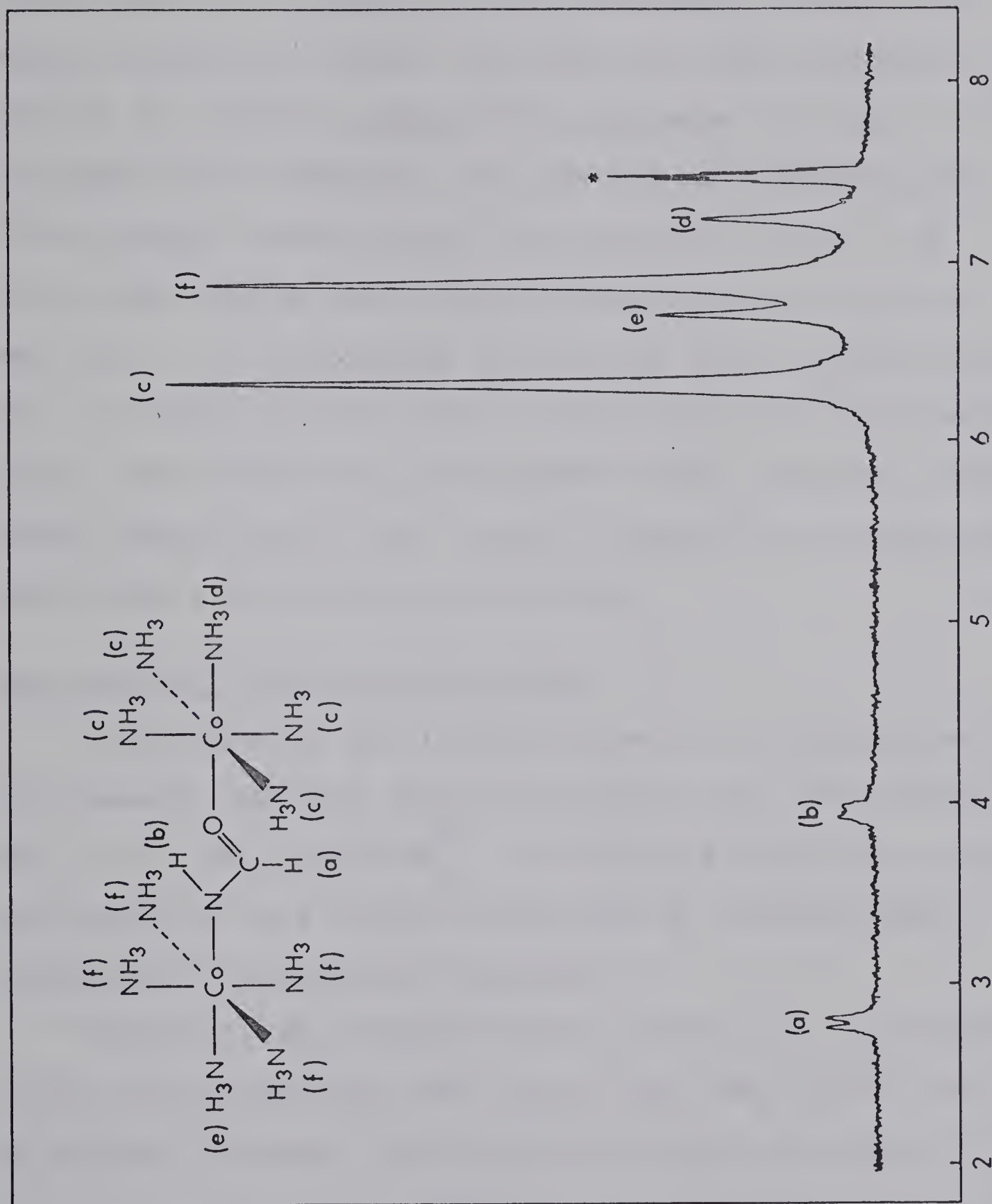


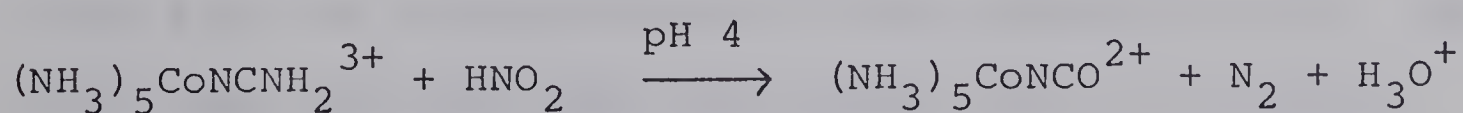
Figure 12. PMR spectrum in d_6 -dimethylsulfoxide of $(\text{NH}_3)_5\text{CoNHCHOCO}(\text{NH}_3)_5^{5+}$ (at 100 MHz).

experiments, with a coupling constant of 5 Hz. It is difficult to decide which pentaamminecobalt(III) unit is associated with a particular NH_3 resonance. However, if we are allowed to extend the empirical rule discussed earlier to include a trans minus cis value of -0.20τ for nitrogen bonded complexes then the ammine resonances due to the oxygen bonded Co(III) unit are at 6.37 and 7.26 τ while those due to the nitrogen bonded unit are at 6.73 and 6.94 τ . If the amines at 6.37 and 6.73 τ , and at 6.94 and 7.26 were from the same Co(III) then this would necessitate both units being coordinated to the nitrogen. This latter possibility is not likely in view of the large steric requirements for such an arrangement.

Reactions of Coordinated Cyanamide

The nature of the linkage isomer of the cyanamide complex remains somewhat uncertain although all indications are that it is $(\text{NH}_3)_5\text{CoN}\equiv\text{C}-\text{NH}_2^{3+}$. It was felt that this assignment could be more firmly established by studying some reactions of coordinated cyanamide.

Initially the reaction with nitrous acid was studied. It was anticipated that this might give $(\text{NH}_3)_5\text{CoNC}^{2+}$ and N_2O as products, however the reaction actually proceeds as

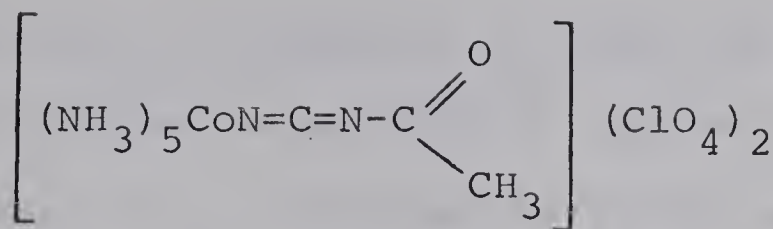


A solution containing 0.02 g NaNO_2 , 0.10 g

$((\text{NH}_3)_5\text{CoNCNH}_2)(\text{ClO}_4)_3$ in 6 ml of H_2O at pH 4 (sodium acetate-acetic acid buffer) was allowed to stand at room temperature for 20 min and then solid NaClO_4 was added to precipitate the product. The $((\text{NH}_3)_5\text{CoNCO})(\text{ClO}_4)_2$ product was characterized by its visible, nmr and infrared spectrum and also by its hydrolysis reaction to $\text{Co}(\text{NH}_3)_6^{3+}$ in 0.1 M HCl (to be described in Chapter IV).

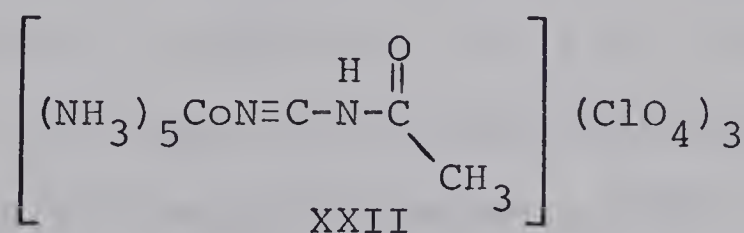
The nitrosation is assumed to proceed by reaction of NO^+ with the NH_2 group of cyanamide. This reaction may generate $(\text{NH}_3)_5\text{CoNC}^{4+}$ as an intermediate which reacts with water to give the cyanato product. It is also possible that direct oxygen atom transfer from NO^+ to cyanamide may occur to give $(\text{NH}_3)_5\text{CoNCO}^{2+}$ as the immediate product.

The acylation of coordinated cyanamide by acetic anhydride has also been observed. This reaction proceeds smoothly and appears to be complete in a few minutes when 0.2 ml of acetic anhydride is added to 0.55 g of $((\text{NH}_3)_5\text{CoNCNH}_2)(\text{ClO}_4)_3$ and ~15 drops of *N,N*-dimethylbenzylamine dissolved in 5 ml of *N,N*-dimethylformamide. The product was isolated by addition of *sec*-butyl alcohol and ether to the reaction solution. The product was then purified by cation exchange chromatography on Rexyn 102(H) weak acid ion exchange resin in the sodium ion form. The main band was moved down the column with 0.4 M sodium acetate which indicated that the complex had a 2+ charge. The product XXI was characterized by its pmr spectrum



XXI

(in d_6 -DMSO) which showed CH_3 protons at 8.17 τ , cis NH_3 protons at 6.38 τ , and trans NH_3 protons at 6.88 τ . The product showed no NH_2 proton resonance and did not change color on changing from neutral to basic solution, both properties which distinguish it from the cyanamide complex. The infrared spectrum shows a strong peak at 2230 cm^{-1} as might be expected for an $-\text{N}=\text{C}=\text{N}-$ system as in the N-cyano-guanidine complex (Table 3). The $\text{C}=\text{O}$ stretching frequency is apparently hidden under the broad NH_3 absorption in the $1600 - 1650\text{ cm}^{-1}$ region. It was also found that the product XXII was obtained when XXI was dissolved in H_2O and concentrated perchloric acid added until precipitation occurred. The pmr spectrum was relatively unchanged and



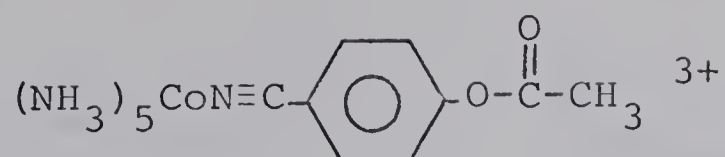
the N-H proton could not be detected presumably because of exchange with water in the solvent or because it was hidden under the broad NH_3 resonance. The infrared spectrum had an absorption band at 2335 cm^{-1} (shoulder at 2300 cm^{-1}) which was much less intense than for XXI. The high energy

shift and loss in intensity is expected for a change from an $-N=C=N-$ system to an $-N\equiv C-\overset{H}{N}-$ system. The $C=O$ stretching frequency now is shifted to higher energy and is observed at 1765 cm^{-1} as expected since the conjugated chain has been broken.

The observation that the acylation reaction proceeds so easily is indicative of the $(\text{NH}_3)_5\text{CoN}\equiv\text{C}-\text{NH}_2$ linkage isomer. The reaction at a coordinated NH_2 is expected to be sterically unfavourable, but it is not impossible. The nitrosation reaction however provides strong evidence for the proposed linkage isomer since the NH_2 isomer should yield $(\text{NH}_3)_5\text{CoOH}_2^{3+}$ as a product rather than the observed $(\text{NH}_3)_5\text{CoNCO}^{2+}$.

Reactions of Coordinated 4-Cyanophenol

The acylation of coordinated 4-cyanophenol was studied in the hope of preparing new complexes suitable for remote attack. The reaction proceeds cleanly when ~ 0.2 ml of acetic anhydride is added to 0.35 g of $((\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{OH})-(\text{ClO}_4)_3$ and ~ 25 drops of N,N -dimethylbenzylamine dissolved in ~ 3 ml of N,N -dimethylformamide. After about two minutes the DMF solution is added to 100 ml of sec -butyl alcohol and 50 ml of anhydrous ether which causes precipitation of the product in easily filtered particles. An nmr spectrum of the filtered product indicated that the reaction had proceeded quantitatively to yield XXIII. The pmr spectrum (in d_6 -DMSO) had a CH_3 resonance at $7.67\text{ }\tau$,

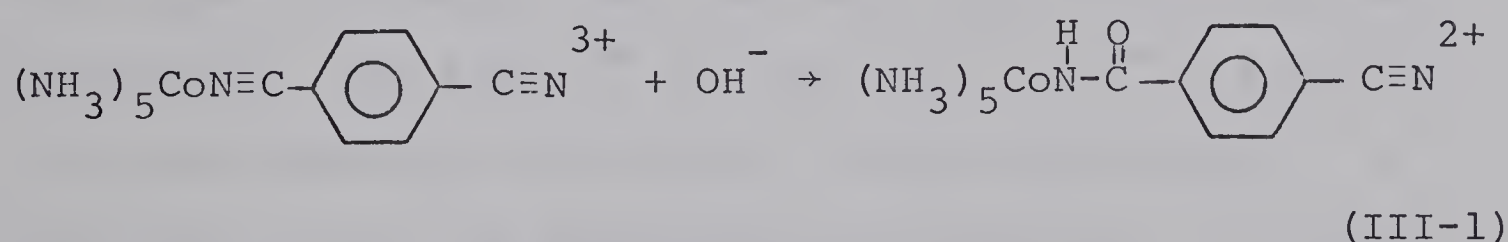


XXIII

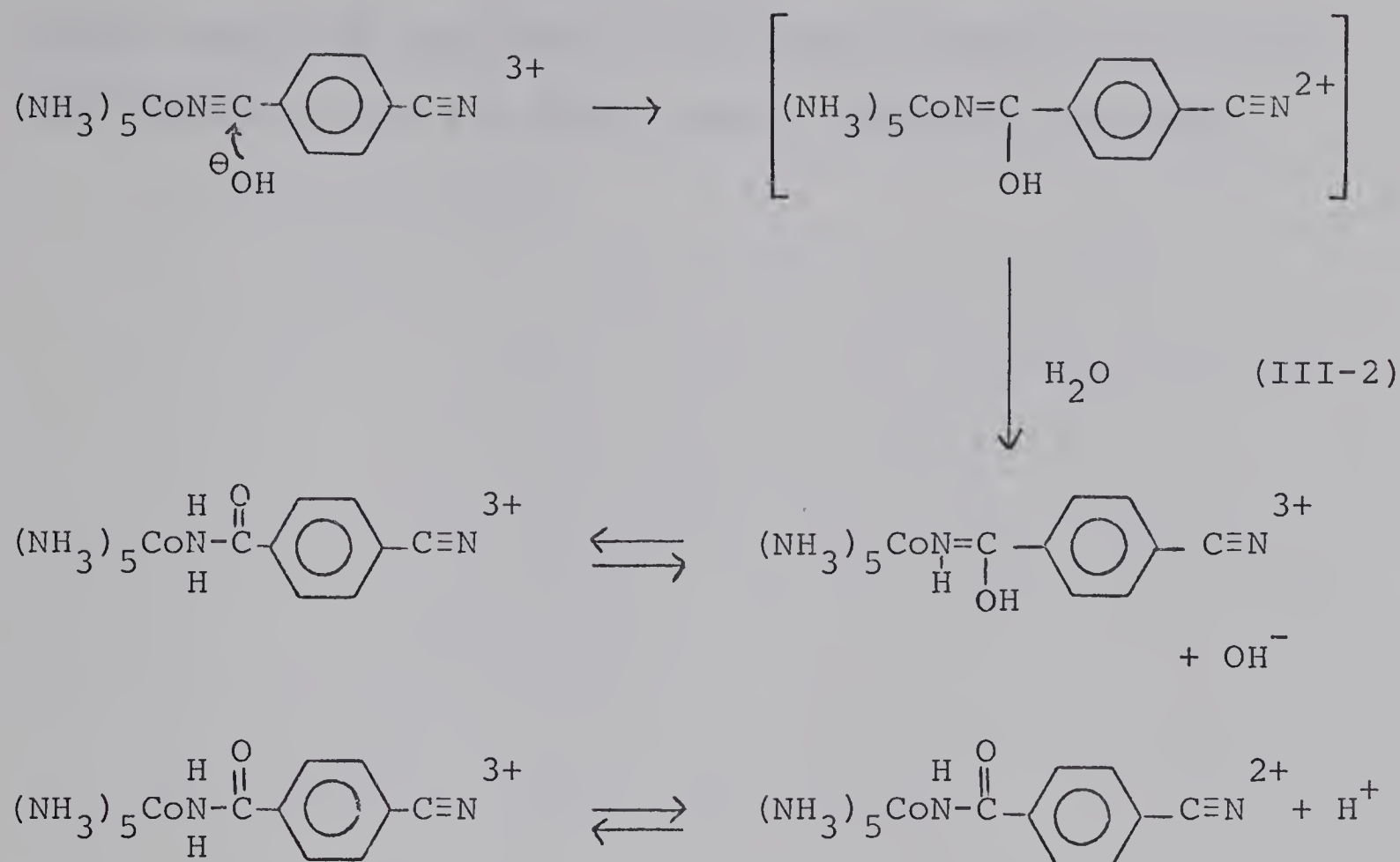
trans NH_3 at 6.58 τ , cis NH_3 at 6.14 τ , and the aryl protons were essentially a quartet centred at 2.18 τ . The ir spectrum showed the nitrile stretching frequency at 2290 cm^{-1} (compared to 2280 cm^{-1} for the parent phenol complex) and C=O stretching frequency at $\sim 1755 \text{ cm}^{-1}$.

Hydrolysis of Coordinated Nitriles

As noted in the experimental section the hydrolysis of coordinated terephthalonitrile to a coordinated amide has been observed at pH 8. Reaction (III-1)



has also been observed for the nitrile-coordinated complexes of 3- and 4-cyanophenol and 4-cyanobenzaldehyde. Preliminary stopped flow measurements on the 3-cyanophenol complex indicate that the reaction is first-order in hydroxide ion with a rate constant of $4.7 \text{ M}^{-1}\text{sec}^{-1}$, ionic strength 1.0 M (NaClO_4) at 29° .⁴⁵ The observations are consistent with attack of hydroxide ion on the nitrile carbon as shown in (III-2).



This type of behavior has also been observed by Breslow, Fairweather, and Keana⁴⁶ for the Cu^{2+} -, Ni^{2+} -, and Zn^{2+} -catalyzed hydration of 2-cyano-1,10-phenanthroline. In the latter study two mechanisms are possible; (1) attack of external hydroxide on the complexed substrate, and (2) attack of a coordinated hydroxide on the complexed substrate. The authors present arguments in favour of mechanism (1). In the case of reaction (III-1) only mechanism (1) is possible. The rates obtained in the phenanthroline nitrile reaction were $\sim 10^4$ times faster than in the 4-cyanophenol case and may indicate that mechanism (2) is operative.

For the terephthalonitrile complex, changes in the

visible spectrum consistent with amide formation have also been observed in 0.1 M HClO_4 over a period of 24 hours.

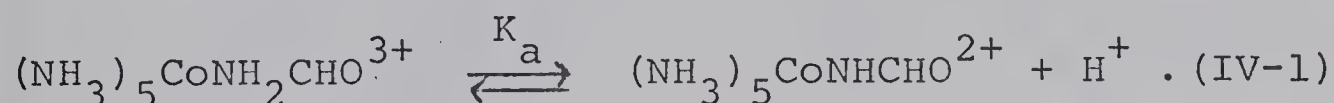
R E S U L T S

Chapter IV

1. Ionization Constants

Acid Dissociation Constant of $(\text{NH}_3)_5\text{CoNH}_2\text{CHO}^{3+}$

The effect of changing hydrogen ion concentration on the spectrum of the N isomer of formamidopentaammine-cobalt(III) is shown in Figure 13 (see Figure 1, chapter III for the complete spectrum). This change is interpreted in terms of the equilibrium



For a system such as this it is shown in Appendix A that a plot of $(\epsilon_{\text{obs}} - \epsilon_2)(\text{H}^+)$ versus ϵ_{obs} should be linear with slope $(-K_a)$ and intercept $(K_a \epsilon_1)$, where ϵ_1 and ϵ_2 are the molar extinction coefficients of the base and acid forms of the complex, and ϵ_{obs} is obtained in the usual way from the observed absorbance and the total complex concentration. The appropriate plot of the data in Appendix B, Table B-1 at 25.5° is shown in Figure 14. Somewhat different values of K_a were obtained from plots at other wavelengths; for example, data at 366.4 nm gave a $\text{p}K_a$ of 2.21 compared to 2.16 obtained at 318.4 nm. The latter value is considered more reliable because there is a larger absorbance change at 318 nm. At 34.6° and 44.4° the $\text{p}K_a$'s are 2.27 and 2.36 respectively. The enthalpy and entropy are $-4.6 \text{ kcal mole}^{-1}$ and -25 eu .

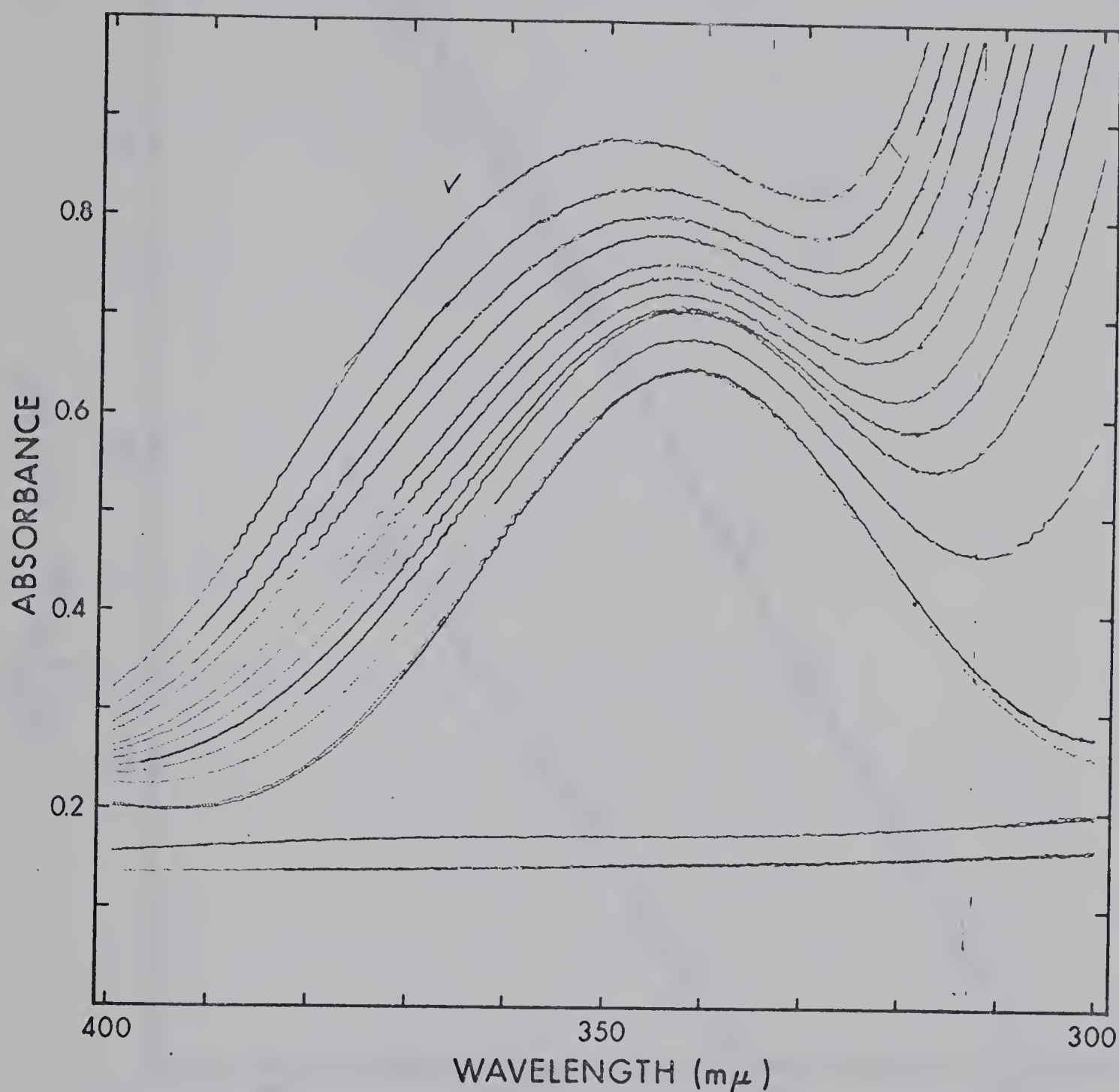


Figure 13. Absorption spectrum of $(\text{NH}_3)_5\text{CoNHCHO}^{2+}$ at 25.5° , ionic strength 0.92 M (LiClO_4) and varying HClO_4 . The absorbance decreases as $[\text{H}^+]$ increases. Curves shown cover the range from 0.0015 to 0.923 M HClO_4 .

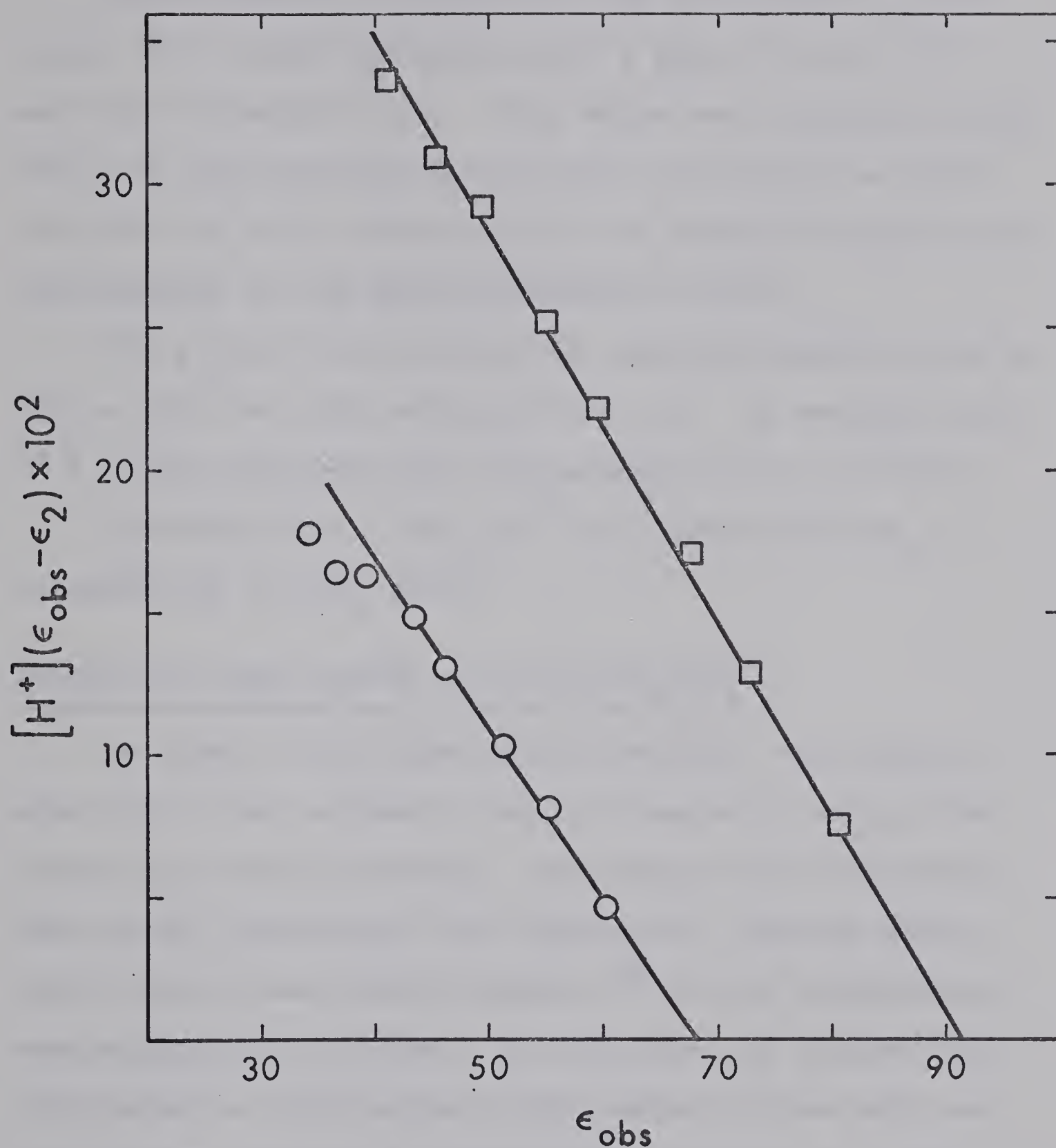


Figure 14. Determination of the acid dissociation constant (K_a) for $(NH_3)_5CoNH_2CHO^{3+}$ from the change in absorbance at 318.4 nm (\square) and 366.4 nm (\circ) at 25.5°C; ionic strength, 0.92 M ($LiClO_4$). ϵ_2 is the molar extinction coefficient of $(NH_3)_5CoNH_2CHO^{3+}$ and ϵ_{obsd} is the observed molar extinction coefficient.

Potentiometric titration of the acid form of the N isomer with sodium hydroxide gave a pK_a of 2.4 at 25° and ionic strength 0.1 M. This value was determined from the pH at half-neutralization and is therefore not very reliable for such a strong acid, but does give qualitative confirmation of the spectrophotometric value.

The pK_a was also determined spectrophotometrically at 349 nm and low ionic strength (0.06 M). An average value of 1.63 was obtained from two determinations at 25.5°C.

Coordination to $(NH_3)_5Co^{3+}$ has changed the pK_a of formamide by >13 pK_a units.

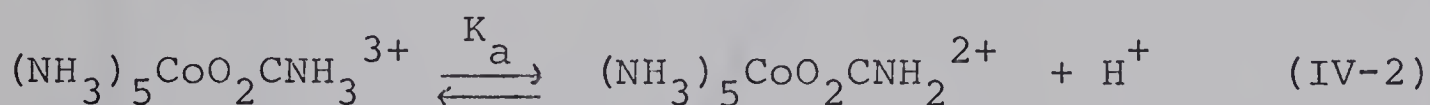
Protonation Equilibrium of $(NH_3)_5CoO_2CNH_2^{2+}$

As noted in the experimental section, the visible spectrum of the carbamate complex changes on going from neutral to acidic solution. The changes are reversible and are not associated with hydrolysis. Similar observations have been made by Barrett¹⁸ in the acetatopentamminecobalt(III) system. In this case the changes were attributed to protonation of the acetate ligand with an equilibrium constant for proton dissociation of 4.0 M (25°, 1.0 M $LiClO_4 - HClO_4$). Likewise, in the less analogous $(OH_2)_5CrO_2CCH_3^{2+}$ system, Deutsch and Taube⁴⁶ observed a protonation equilibrium with a dissociation constant of 3.25 M at 25° and ionic strength 4.0 M. However, in neither case was it possible to decide which

of the ligand oxygen atoms was being protonated.

A similar protonation is assumed for the carbamate ligand, and in this case it is possible to infer at least, which of the ligand atoms is protonated. It was found that the carbamate -NH_2 protons did not exchange with D_2O in neutral or basic solution, however in acidic D_2O exchange does occur and the -NH_2 pmr is broadened. This shows that the -NH_2 proton exchange is acid catalyzed and provides evidence that protonation of the complex occurs on the -NH_2 group of the carbamate ligand.

The equilibrium constant for the reaction



has been determined spectrophotometrically at 25.8°C and 290 nm. It can be shown that a plot of $(\epsilon_1 - \epsilon_{\text{obs}})/[\text{H}^+]$ versus ϵ_{obs} should be linear with slope K_a^{-1} and intercept (ϵ_2/K_a) , where ϵ_1 and ϵ_2 are the molar extinction coefficients of unprotonated and protonated complexes, and ϵ_{obs} is obtained from the measured absorbance and total complex concentration at a particular hydrogen ion concentration. The resulting plot is linear, as shown in Figure 15, and gives $K_a = 0.105 \text{ M}$, and $\epsilon_2 = 7.7 \text{ l mole}^{-1} \text{ cm}^{-1}$.

Proton Dissociation from Cyanamidopentaamminecobalt(III).

The changes in the visible spectrum of the cyanamide

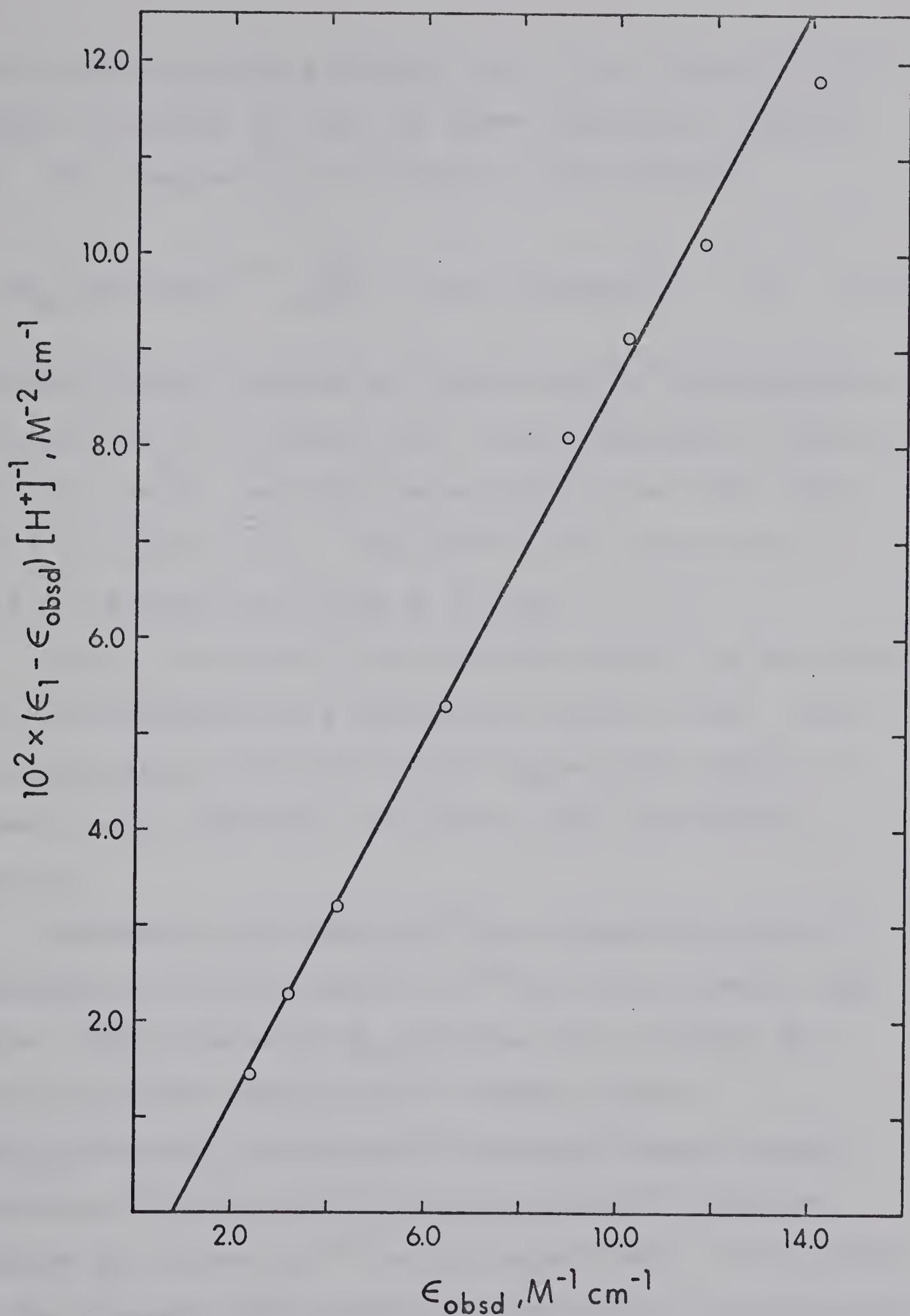
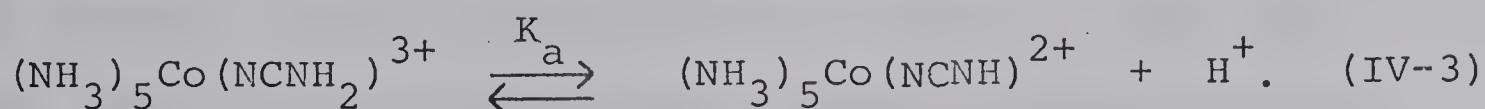


Figure 15. Spectrophotometric determination of the acid dissociation constant of $(\text{NH}_3)_5\text{CoO}_2\text{CNH}_3^{3+}$ at 290 nm, 25.8° and ionic strength 1.0 M (LiClO_4). ϵ_1 is the molar extinction coefficient of the unprotonated species.

complex when the pH is changed from ~8 to 0 have been discussed in Chapter III and are shown in Figure 2 chapter III. The changes are attributed to the reaction



The equilibrium constant was determined by potentiometric titration in 1.0 M LiClO_4 with sodium hydroxide. The pK_a 's at 24.6° , 34.8° , and 43.8° were found to be 5.18, 4.95, and 4.74 respectively. The enthalpy and entropy are $10.0 \pm 0.5 \text{ kcal mole}^{-1}$ and $10 \pm 2 \text{ eu}$.

In all titrations the equivalent weight was determined to be 520 compared to a theoretical value of 486. This indicates about 6-7% of the N-cyanoguanidine complex is present as an impurity, as noted in the experimental section.

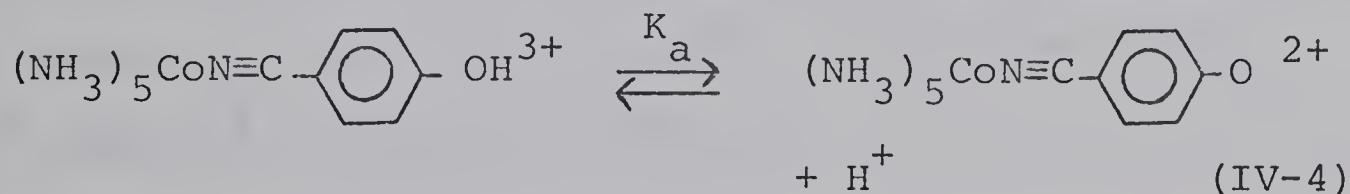
Coordination to $(\text{NH}_3)_5\text{Co}^{3+}$ has changed the pK_a of cyanamide (at 25°C) from 10.27²⁹ to 5.18 or about 5 pK_a units. This change in pK_a provides some evidence for formulating the complex as the linkage isomer

$(\text{NH}_3)_5\text{Co}-\text{N}\equiv\text{C}-\text{NH}_2$ since for the nitrogen bonded ligands sulfamate³⁴ and formamide the pK_a of the NH_2 protons changes by >10 and >13⁴⁸ units respectively. The acidity of the cyanamide $-\text{NH}_2$ protons is increased on coordination, presumably because of the increased H_2N to C π -bonding over that present in the free ligand.³⁵

On the other hand it might be argued that the large change in visible spectrum on formation of the conjugate base is more consistent with NH_2 coordination. However, the $\text{C}=\text{N}=\text{NH}^-$ ligand is isoelectronic with N_3^- , NCS^- and NCO^- and it is not unreasonable therefore that it gives a spectrum similar to the $(\text{NH}_3)_5\text{Co}^{3+}$ complexes of these ions. The spectrum of the $\text{N}\equiv\text{C}-\text{NH}_2$ complex is similar to that of other nitrile ligand complexes such as those with acetonitrile and terephthalonitrile.

Acid Dissociation Constant of $(\text{NH}_3)_5\text{CoN}\equiv\text{C}-\text{C}_6\text{H}_4-\text{OH}^{3+}$

The equilibrium constant for reaction (IV-4)



has been measured at 25° in H_2O by potentiometric titration with sodium hydroxide. The $\text{p}K_a$ determined from the pH at half neutralization was found to be 6.62 compared to 7.95 for the free ligand.⁴⁹ The change in the $\text{p}K_a$ of the complexed ligand with respect to the free ligand can be attributed to the electron withdrawing effect of the $(\text{NH}_3)_5\text{Co}^{3+}$.

2. Acid Hydrolysis of $(\text{NH}_3)_5\text{CoNCO}^{2+}$

Preliminary observations indicated that $(\text{NH}_3)_5\text{CoNCO}^{2+}$ decomposes to $\text{Co}(\text{NH}_3)_6^{3+}$ and CO_2 in acidic solution. The

$\text{Co}(\text{NH}_3)_6^{3+}$ product was identified by comparison of the visible, infrared, and pmr spectra to those of an authentic sample, and also by C, H, N analysis.

The kinetics of the decomposition of $(\text{NH}_3)_5\text{CoNCO}^{2+}$ were studied at 5.0° , 15.0° , and 25.0° in 0.021 to 0.217 M HClO_4 , at an ionic strength of 1.0 M, adjusted with LiClO_4 . The results are given in Table B-2 Appendix B. The rate of disappearance is given by

$$-\frac{d(\ln[(\text{NH}_3)_5\text{CoNCO}^{2+}])}{dt} = k_o = k_1[\text{H}^+].$$

The rate constant k_1 was determined at each temperature from the slope of a plot of k_o vs $[\text{H}^+]$. The values of k_1 , ΔH_1^\ddagger and ΔS_1^\ddagger are given in Table 5.

3. Chromium(II) Studies: Kinetics and Product Analysis Oxygen-Bonded Complexes of Formamide, N,N-dimethyl- formamide, and Urea.

The reductions of the formamide, DMF, and urea complexes were shown to consume one mole of chromium(II) per mole of cobalt(III) complex. Solutions initially containing between 3:1 and 5:1 ratios of reductant to oxidant were analyzed for excess chromium(II) after ten half-times for reaction.

The rates of reduction were found to be independent of hydrogen ion concentration and obey the rate law

Table 5

KINETIC PARAMETERS FOR ACID HYDROLYSIS OF ISOCYANATOPENTA-
AMMINECOBALT(III).

Temp °C	k_1 $M^{-1} \text{ sec}^{-1}$	ΔH^\ddagger kcal mole^{-1}	ΔS^\ddagger eu
5.0	0.029		
15.0	0.078		
25.0	0.162	13.1 ± 0.5^a	-18 ± 2^a

a

Errors are estimated assuming a $\pm 3\%$ error on the rate constant k_1 as shown by maximum deviations in the slope of a plot of k_0 versus $[H^+]$.

$$-\frac{d(\ln[\text{cobalt(III) complex}])}{dt} = k'' [\text{Cr}^{2+}] .$$

The rate data for these complexes are given in Table B-3, Appendix B. The rate constants and activation parameters are given in Table 6.

The identification of the initial product of the reactions is most crucial in determining the point of attack of the reducing agent on the ligands. For the formamide complex, repeated scans of the visible spectrum for reactants at approximately 1:1 concentrations (Figure 16) showed the growth of two maxima at 408 and 575 nm, which did not lose intensity with time. Four isosbestic points at 388, 432, 573, and 642 nm further confirm the existence of only one product. The product was isolated by ion exchange chromatography and shown to be $\text{Cr}(\text{OH}_2)_6^{3+}$ by its visible absorption spectrum. Such results are not consistent with hydrolysis of an initial Cr(III)-O isomer product unless such hydrolysis is very fast.

Similar behavior was found for the DMF and urea complexes, the product after ion-exchange being $\text{Cr}(\text{OH}_2)_6^{3+}$. For the DMF complex three good isosbestic points were observed at 387, 437, and 573 nm. The results for the DMF complex are consistent with the previous work of Gould.⁵⁰ The urea complex showed isosbestic points at 394, 428, and 603 nm for a run with initial concentrations

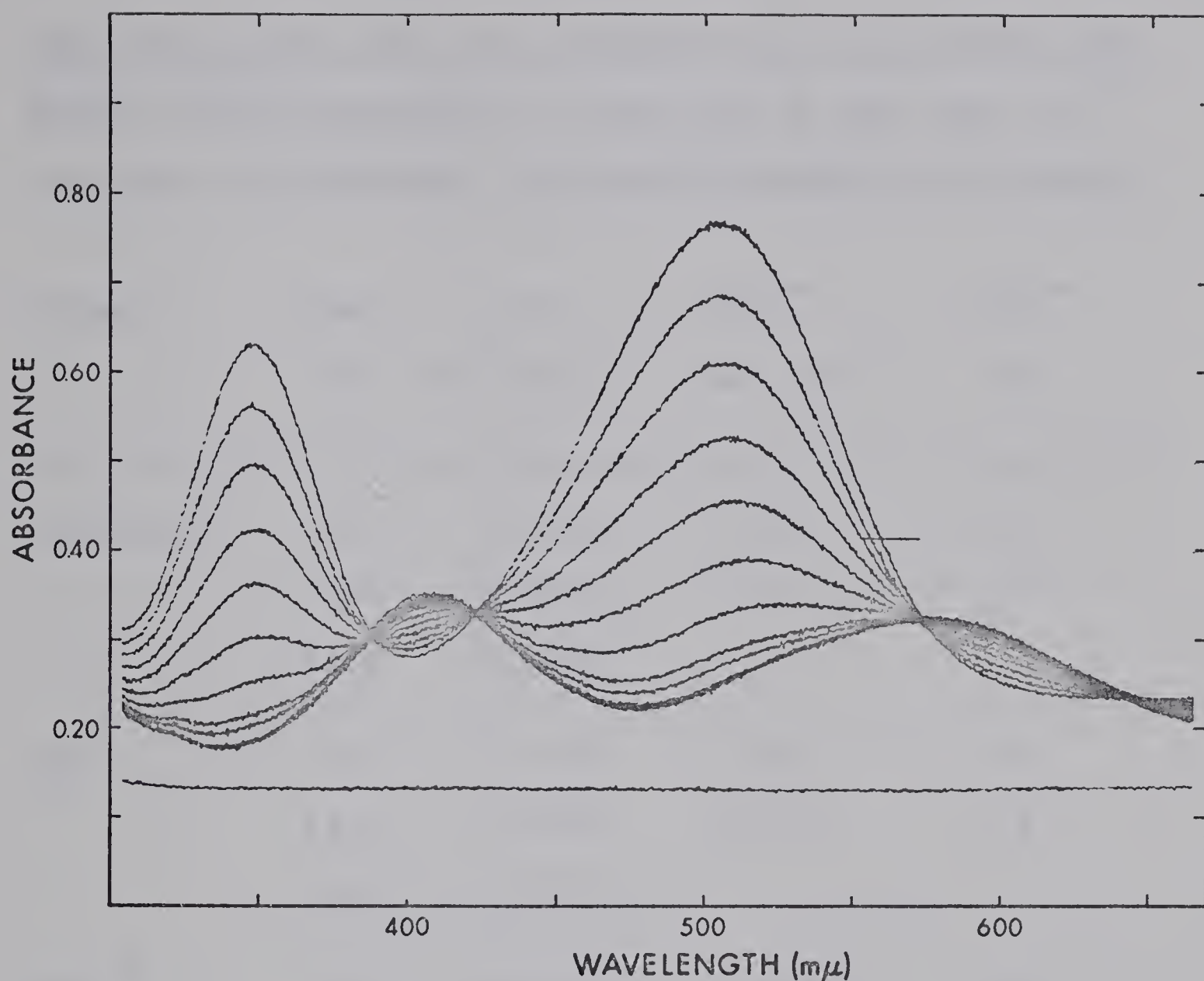


Figure 16. Change in visible spectrum during reduction of $(\text{NH}_3)_5\text{CoOCHNH}_2^{3+}$ (0.011 M) by chromium(II) (0.019 M); $[\text{H}^+] = 0.505 \text{ M}$; 28.5° ; ionic strength 0.99 M (LiClO_4). The absorbance is decreasing at $\sim 500 \text{ nm}$ and $\sim 350 \text{ nm}$ due to consumption of Co^{3+} complex, and increasing at $\sim 575 \text{ nm}$ and $\sim 410 \text{ nm}$ due to production of $\text{Cr}(\text{OH}_2)_6^{3+}$. Isosbestic points occur at 388, 432, 573, and 642 nm. The spectral scans were started at 4, 22, 45, 80, 121, 180, 262, 460, 645, 763, and 1436 min after mixing. The last three show no change.

Table 6

OBSERVED SECOND ORDER RATE CONSTANTS AND ACTIVATION PARAMETERS FOR THE CHROMIUM(II) REDUCTION OF THE $(\text{NH}_3)_5\text{Co}^{3+}$ COMPLEXES OF FORMAMIDE, N,N-DIMETHYLFORMAMIDE, AND UREA.

Ligand	Temp °C	k" $\text{M}^{-1} \text{sec}^{-1}$	ΔH^\ddagger ^a kcal mole ⁻¹	ΔS^\ddagger ^a eu
Formamide ^b	25.0	0.0085	10.7	-32
	36.0	0.0159	± 1.0	± 3
	46.0	0.0296		
DMF ^b	32.6	0.0079	10.6	-33
	44.6	0.0160	± 1.0	± 3
	54.1	0.0257		
Urea ^b	24.6	0.0193	10.6	-31
	34.8	0.345	± 1.0	± 3
	45.0	0.0646		

^a Errors are estimated assuming a $\pm 5\%$ error on the rate constants.

^b The ligands are all coordinated through the carbonyl oxygen atom.

of $[\text{Cr}^{2+}] = 0.031 \text{ M}$, $[\text{Co}^{3+}] = 0.00195 \text{ M}$, and $[\text{H}^+] = 0.248 \text{ M}$.

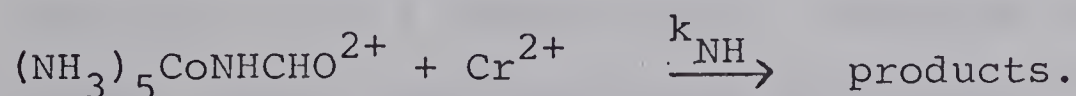
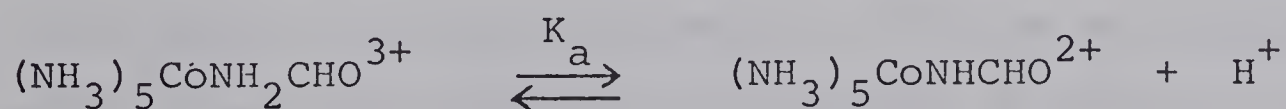


The stoichiometry of the reduction of the N isomer of formamidopentaamminecobalt(III) was shown to be one mole of chromium(II) per mole of cobalt(III) by analyzing for the chromium(II) remaining after ten half-times for reaction solutions containing various initial chromium(II) to cobalt(III) ratios. The analysis was carried out by oxidation of chromium(II) with excess iron(III) and determining the excess iron(III) iodometrically.

The reduction of the N isomer was found to follow the rate law

$$-\frac{d \ln [(\text{NH}_3)_5\text{CoNH}_2\text{CHO}^{3+}]}{dt} = \frac{k' [\text{Cr}^{2+}]}{[\text{H}^+]} \quad (\text{IV-5})$$

A summary of representative rate data is given in Table B-4 of Appendix B. The plot of $k'/[\text{H}^+]$ vs $[\text{H}^+]^{-1}$ shown in Figure 17 is linear as predicted by equation (IV-5). This rate law is consistent with the mechanism



The products are $\text{Co}^{2+}(\text{aq})$, NH_4^+ , and a chromium(III) complex,

which is not $\text{Cr}(\text{OH}_2)_6^{3+}$, as shown by ion exchange experiments discussed later. This mechanism gives the rate law

$$-\frac{d \ln[(\text{NH}_3)_5\text{CoNH}_2\text{CHO}]}{dt} = \frac{k_{\text{NH}}K_a}{K_a + [\text{H}^+]} [\text{Cr}^{2+}]. \quad (\text{IV-6})$$

Under the conditions of the kinetic study $[\text{H}^+] \gg K_a$; therefore by comparison of equation (IV-5) and (IV-6), $k' = k_{\text{NH}}K_a$. The specific rate constant k_{NH} has been determined from the experimental values of k' and K_a at different temperatures. The results along with the activation parameters are given in Table 7.

An acid-independent term in the rate law for reduction of the N isomer could correspond to the rate of reduction of $(\text{NH}_3)_5\text{CoNH}_2\text{CHO}$ (k_{NH_2}). This term would appear as the intercept on a plot such as Figure 17. A least-squares analysis of the data indicates that k_{NH_2} is less than $1 \times 10^{-3} \text{ M}^{-1} \text{ sec}^{-1}$, and cannot be reliably established.

Progress of the reduction was followed by repeatedly scanning the visible region of the spectrum. It was found that a maximum absorbance at 410 nm was reached, which then lost intensity and shifted to 408 nm. This indicates that a chromium(III) formamide complex is being formed, which then hydrolyzes to $\text{Cr}(\text{OH}_2)_6^{3+}$. These observations permitted the choice of optimum reactant

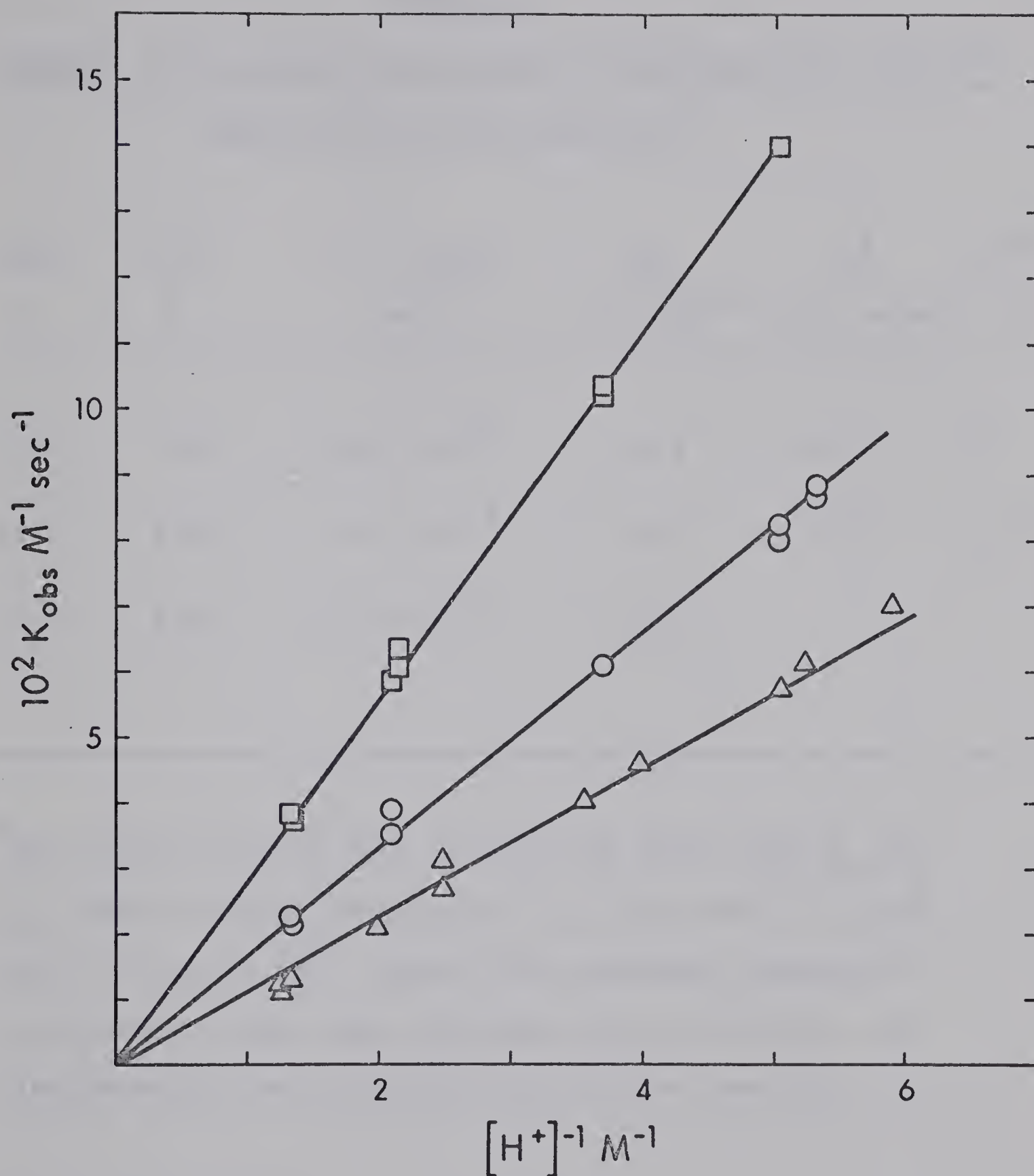


Figure 17. Dependence of reduction rate of $(\text{NH}_3)_5\text{CoNH}_2\text{CHO}^{3+}$ by Cr^{2+} on $[\text{H}^+]$, ionic strength 0.92 M (LiClO_4): Δ 25.5°; O, 34.6°; \square 44.4°.

Table 7SUMMARY OF EQUILIBRIUM AND KINETIC PARAMETERS FOR THE Cr^{2+} REDUCTION OF $(\text{NH}_3)_5\text{CoNH}_2\text{CHO}^{3+}$

Temp °C	$10^3 K_a$ M	$k' = k_{\text{NH}} K_a$ sec ⁻¹	k_{NH} M ⁻¹ sec ⁻¹	ΔH^\ddagger kcal mole ⁻¹	ΔS^\ddagger eu
25.5	6.92	1.20×10^{-2}	1.74	12.0	-17
34.6	5.36	1.61×10^{-2}	3.00	$\pm 2.0^a$	$\pm 6^a$
44.4	4.37	2.75×10^{-2}	6.30		

a

The errors in this case include the error from K_a and k_1 , each of which contributes $\sim \pm 1$ kcal mole⁻¹ to ΔH^\ddagger and $\sim \pm 3$ eu to ΔS^\ddagger . Errors are estimated assuming a $\pm 5\%$ error on the rate constants and $\pm 10\%$ on K_a , as indicated by the reproducibility of the results.

concentrations to give the most chromium(III)-formamide product. The product solutions under such conditions were ion exchanged, and the visible spectrum of the chromium (III) product was recorded. Representative results of such experiments are given in Table 8.

The extinction coefficient of the product shows that it is not $\text{Cr}(\text{OH}_2)_6^{3+}$, and the peak positions seem most consistent with those expected for an O-bonded formamide complex. The acid form of the N-bonded isomer would be expected to have a spectrum similar to $(\text{OH}_2)_5\text{CrNH}_3^{3+}$,⁵¹ which has absorption maxima at 547 and 397 nm. This expectation is based on analogy to the spectra of the $(\text{NH}_3)_5\text{Co}$ -formamide isomers and is also consistent with results on the chromium(II)-isonicotinamide system.¹⁴

The chromium-formamide complex was also prepared by the reaction of lead(II) (0.032 M) and chromium(II) (0.067 M) in aqueous formamide (0.075 M). The characteristics of the visible spectrum of the chromium(III) product (obtained after elution from Dowex-50X8) are given in Table 8 and appear identical, within experimental error, with those from the reduction of the N isomer with chromium(II). The same product was also obtained by treating aqueous chromium(III) perchlorate and formamide at room temperature for 3 days and then separating the mixture by ion exchange. A qualitative test⁵² for formamide was positive on the ion exchanged product from all

Table 8ELECTRONIC SPECTRA OF $(\text{OH}_2)_5\text{Cr}^{3+}$ COMPLEXES.

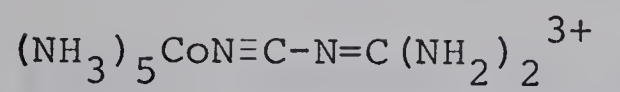
Reaction	λ_{max}		λ_{max}'	
	nm	ϵ_{max}	nm	ϵ_{max}'
$(\text{NH}_3)_5\text{CoO=CHNH}_2^{3+} + \text{Cr}^{2+}$ a	407	15.0	575	12.8
$(\text{NH}_3)_5\text{CoNHCHO}^{2+} + \text{Cr}^{2+}$ b	409	22.3	578	20.5
$\text{Pb}^{2+} + \text{Cr}^{2+} + \text{O=CHNH}_2$	409	21.0	578	19.9
$\text{Cr}(\text{OH}_2)_6^{3+}$ c	408	15.6	574	13.4

a $[\text{Cr}^{2+}]$, 0.115 M; [cobalt(III) complex], 0.009 M; $[\text{H}^+]$, 0.582 M; reacted at 36.0° for 1 hr.

b $[\text{Cr}^{2+}]$, 0.012 M; [cobalt(III) complex], 0.011 M; $[\text{H}^+]$, 0.09 M; reacted at room temperature for 2 hr.

c J. A. Laswick and R. A. Plane, J. Amer. Chem. Soc., 81, 3564 (1959).

three methods of preparation.

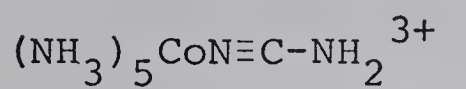


The reduction of the N-cyanoguanidine complex followed the rate law

$$-\frac{d[\ln(\text{cobalt(III) complex})]}{dt} = k''[\text{Cr}^{2+}]$$

The rate data are summarized in Table B-5 of Appendix B. The rate constants and activation parameters are summarized in Table 9.

The chromium(III) product was investigated by scanning the reaction solutions and by ion exchange. Scan runs with chromium(II) in either two or ten fold molar excess over cobalt(III) showed good isosbestic behavior and the final product spectrum did not change with time (up to 24 hours). Ion exchange analysis showed that the product was $\text{Cr}(\text{OH}_2)_6^{3+}$, identified by its visible spectrum.



The stoichiometry of the reduction of the cyanamide complex was found to be 1:1, since the visible spectrum showed no unreacted cobalt(III) complex in solutions containing initial 1:1 ratios of oxidant to reductant.

The reduction of cyanamidopentaamminecobalt(III) was found to follow the rate law

Table 9

KINETIC PARAMETERS FOR CHROMIUM(II) REDUCTION OF N-CYANO-
GUANIDINOPENTAAMMINECOBALT(III).

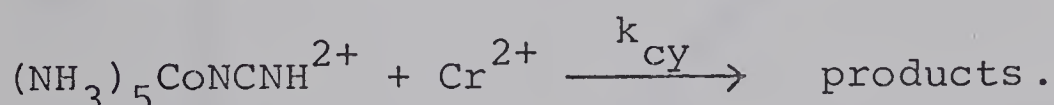
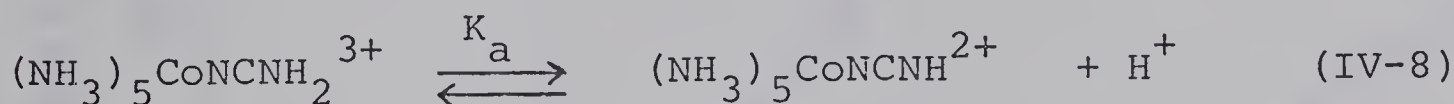
Temp, °C	k'' $M^{-1} \text{ sec}^{-1}$	ΔH^\ddagger kcal mole^{-1}	ΔS^\ddagger eu
24.6	0.0290	8.3	-37
34.8	0.0470	$\pm 1^a$	$\pm 3^a$
43.8	0.0679		

^a Errors are estimated assuming a $\pm 5\%$ error on the rate constants.

$$-\frac{d \ln[(\text{NH}_3)_5\text{CoNCNH}_2^{3+}]}{dt} = \frac{k'}{[\text{H}^+]} [\text{Cr}^{2+}] = k_{\text{obsd}} [\text{Cr}^{2+}]. \quad (\text{IV-7})$$

The kinetics were determined with a large (15 fold) excess of chromium(II) and H^+ to obtain k_{obsd} . Plots of k_{obsd} versus $[\text{H}^+]^{-1}$ are linear as shown in Figure 18. The value of k' was determined from the slope of the lines in Figure 18. It should be noted that no significant intercept could be detected for these lines. A summary of the rate data is given in Table B-6 of Appendix B.

The rate law is consistent with the reaction scheme



If it is assumed that the first step is a rapid equilibrium, then

$$-\frac{d \ln[(\text{NH}_3)_5\text{CoNCNH}_2^{3+}]}{dt} = \frac{k_{\text{cy}} K_a}{K_a + [\text{H}^+]} [\text{Cr}^{2+}]. \quad (\text{IV-9})$$

K_a has been determined as described previously and is always less than $[\text{H}^+]$ therefore comparing equations (IV-7) and (IV-9), $k' = k_{\text{cy}} K_a$. Values of k' , K_a , and k_{cy} are summarized in Table 10.

The chromium(III) product of the reduction of the cyanamide complex appears to be $\text{Cr}(\text{OH}_2)_6^{3+}$. This seems unusual in that the rate law and large specific rate constant k_{cy} both indicate a bridging mechanism. In a kinetic

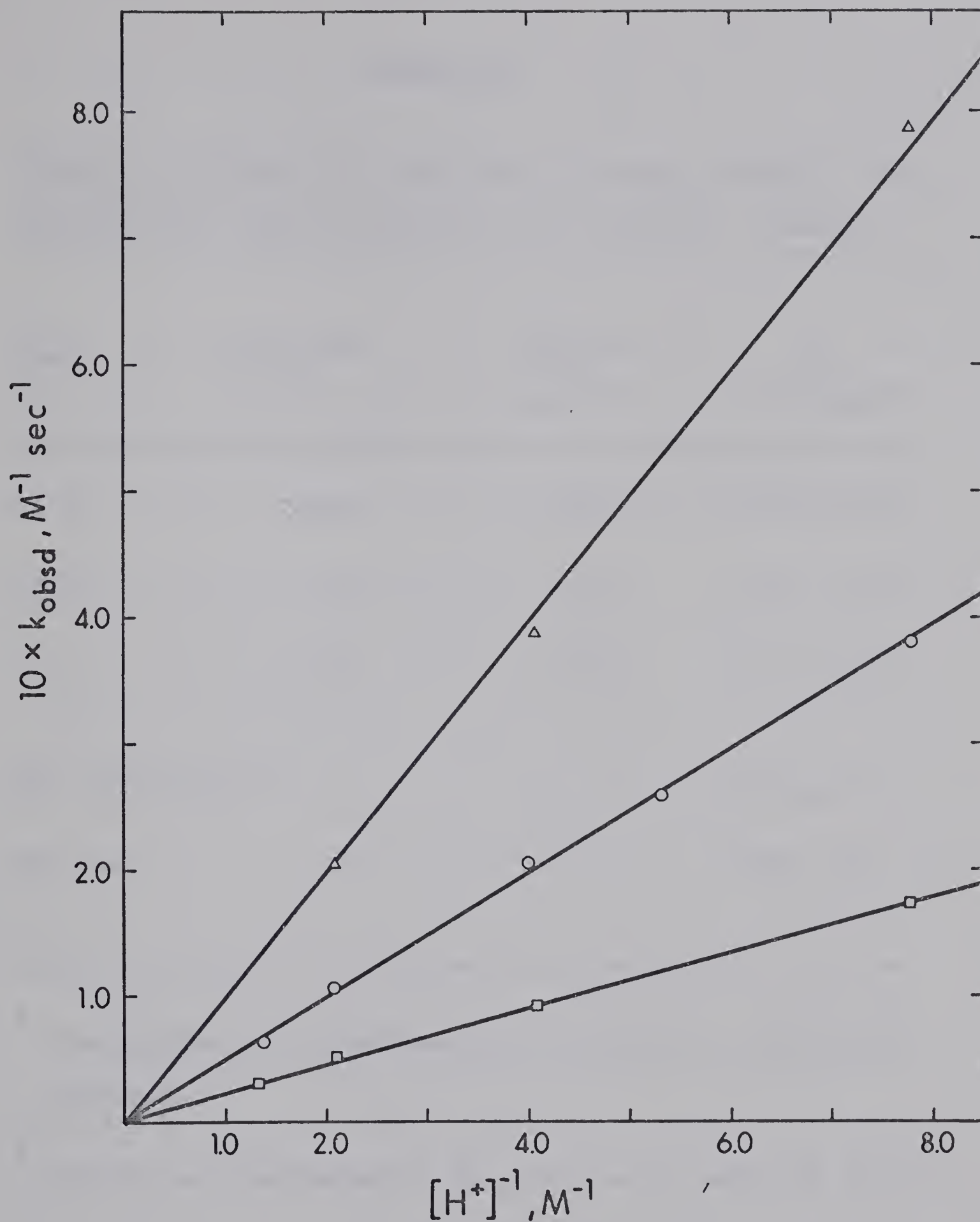


Figure 18. Dependence of the reduction rate of $(\text{NH}_3)_5\text{CoNCNH}_2^{3+}$ by Cr^{2+} on $[\text{H}^+]$, ionic strength 1.0 M (LiClO_4): Δ , 43.8°; O, 34.8°; \square 24.6°.

Table 10

KINETIC PARAMETERS FOR REDUCTION OF $(\text{NH}_3)_5\text{CoNCNH}_2^{3+}$ BY
 CHROMIUM(II), IONIC STRENGTH 1.0 M ($\text{LiClO}_4 - \text{HClO}_4$).

Temp °C	$10^5 K_a^{a,b}$ M	$10^2 k' b$ sec^{-1}	k_{cy} $\text{M}^{-1} \text{sec}^{-1}$
24.6	0.66	2.20	3.33×10^3
34.8	1.12	4.93	4.40×10^3
43.8	1.82	9.93	5.46×10^3
ΔH^\ddagger (kcal mole ⁻¹)			4.3 ± 1
ΔS^\ddagger (eu)			-28 ± 3

a
 Determined by potentiometric titration at 1.0M ionic strength.

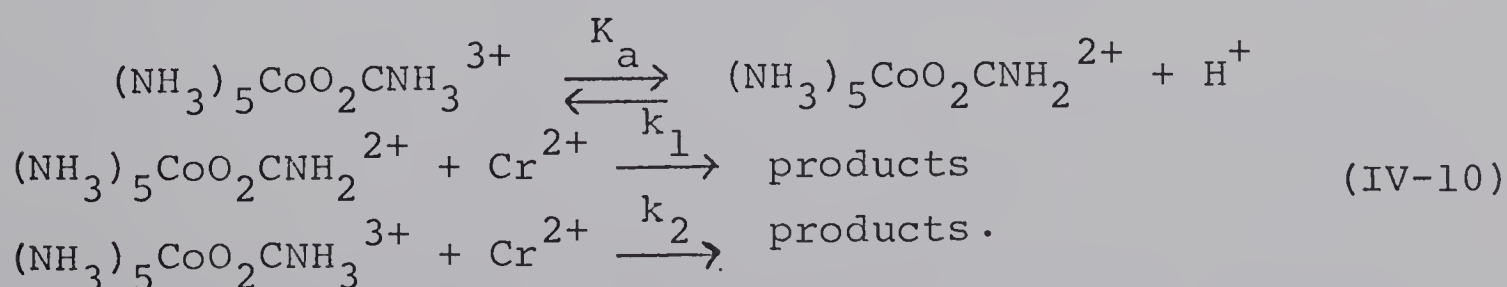
b
 Errors are estimated to be $\pm 10\%$ on K_a and $\pm 5\%$ on k' .

run with initial concentrations of 5.0×10^{-3} M chromium(II), 3.9×10^{-3} M cobalt(III) and 4.8×10^{-2} M H^+ the complete spectrum was scanned at various intervals. Good isosbestic behavior was observed for 95% reaction with isosbestic points at 652, 543, 419 and 381 nm. Ion exchange analysis after complete reaction of a solution with the same composition gave a product with wavelength and extinction coefficient maxima identical with those of $Cr(OH_2)_6^{3+}$. There was no evidence for any chromium(III) cyanamide product.

Carbamatopentaamminecobalt(III)

The stoichiometry of the reduction of the carbamate complex was found to be 1:1, since the visible spectrum showed no unreacted cobalt(III) complex in solutions containing initial 1:1 ratios of oxidant to reductant. In addition the rate constant obtained under second order conditions was in good agreement with those obtained under conditions pseudo-first order in chromium(II).

The rate of reduction of the carbamate complex was found to increase with decreasing acid concentration, eventually levelling off at low $[H^+]$ as shown in Figure 19. This behavior is consistent with the reaction scheme



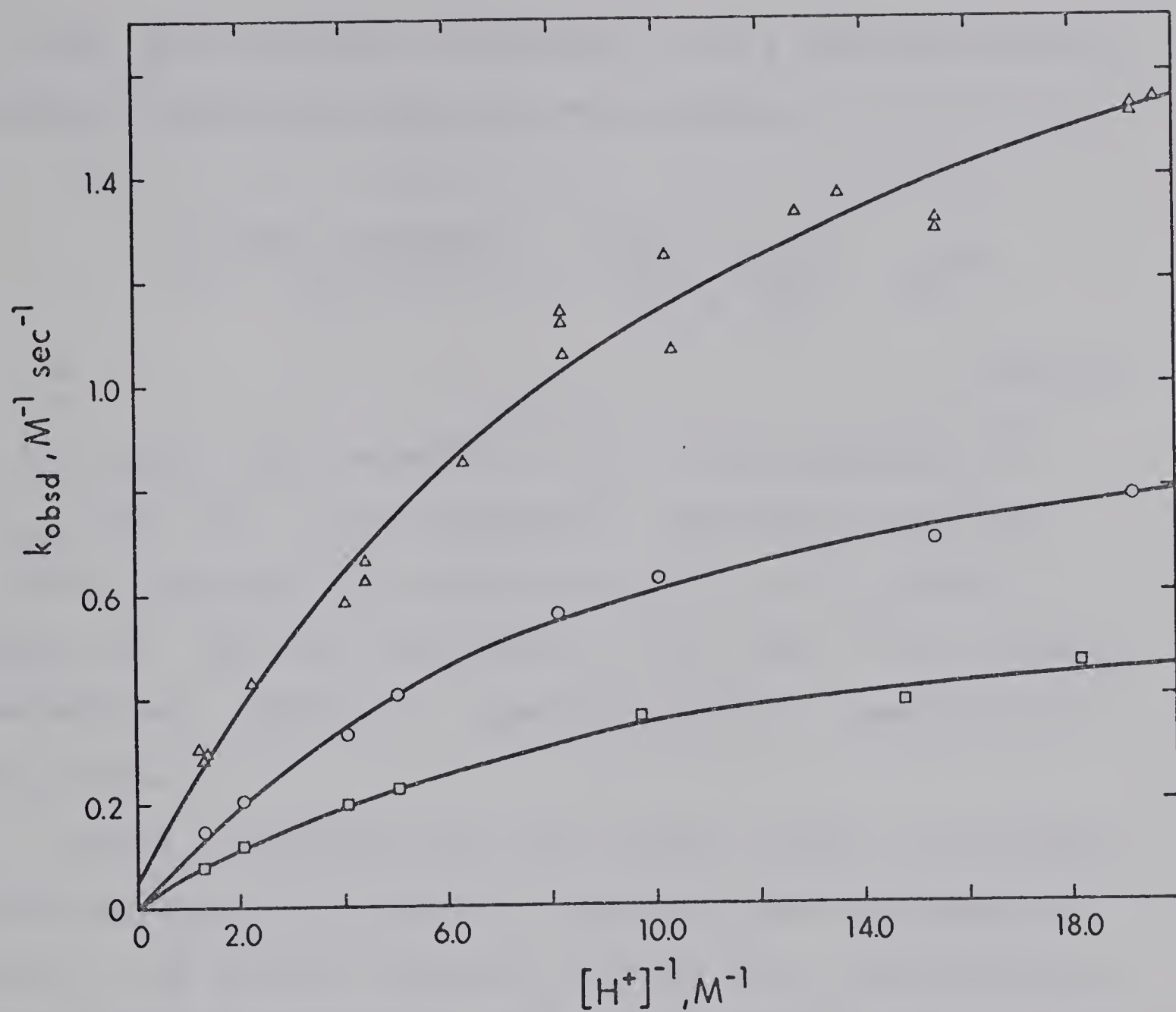


Figure 19. Dependence of the reduction rate of $(\text{NH}_3)_5\text{CoO}_2\text{CNH}_2^{2+}$ by Cr^{2+} on $[\text{H}^+]$, ionic strength 1.0 M (LiClO_4): Δ , 25.8°; O, 15.0°; \square , 8.0°.

If the first reaction is assumed to be a rapid pre-equilibrium, then the rate law for reduction is

$$-\frac{d \ln[(\text{NH}_3)_5\text{CoO}_2\text{CNH}_2]}{dt} = \frac{k_1 K_a + k_2 [\text{H}^+]}{K_a + [\text{H}^+]} [\text{Cr}^{2+}] \quad (\text{IV-11})$$

A non-linear least squares ⁵³ fit of the variation of k_{obsd} with $[\text{H}^+]$ to the expression indicated by equation (IV-11) gave best fit values of k_1 , k_2 , and K_a shown in Table 11. The rate constant k_2 is too small to be reliably established. Table B-7, Appendix B gives a summary of the rate data.

The K_a calculated from the kinetic study is in reasonable agreement with the value measured spectrophotometrically. The kinetic values at 8.0 and 15.0° are considered to be the most reliable, since at 25.8° most of the kinetics were done under second order conditions.

The chromium(III) product of reduction of the carbamate complex has been characterized by ion exchange chromatography and by its visible spectrum. The product shows ion exchange properties typical of a dipositive ion and generally is eluted along with the cobalt(II) ion. It should be noted that only 65% of the total expected product has been obtained as the +2 charged species. The remainder appears to be $\text{Cr}(\text{OH}_2)_6^{3+}$, which may result from hydrolysis

Table 11KINETIC PARAMETERS FOR REDUCTION OF CARBAMATOPENTAAMINE-COBALT(III) BY CHROMIUM(II), IONIC STRENGTH 1.0M(LiClO₄ - HClO₄).

Temp °C	K_a^a M	k_1^a $M^{-1} \text{sec}^{-1}$	k_2^a $M^{-1} \text{sec}^{-1}$
8.0	0.111 (0.097→0.131)	0.68 (0.62→0.73)	-0.01 (-0.05→0.13)
15.0	0.113 (0.103→0.124)	1.15 (1.10→1.20)	-0.01 (-0.05→0.03)
25.8	0.085 (0.078→0.094) ^b	2.42 (2.31→2.54)	0.05 (-0.03→0.13)
	ΔH^\ddagger (kcal mole ⁻¹)	11.4 \pm 0.4	----
	ΔS^\ddagger (eu)	-18.6 \pm 2	----

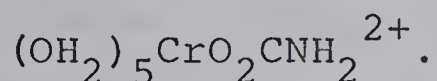
a Error limits approximate the 95% confidence limits.

b A value of 0.105 M was determined spectrophotometrically.

on the ion exchange column or may be a direct product of the reduction.

A sample of the chromium(III) product free of cobalt(II) was obtained from a reaction solution initially containing 0.0189 M cobalt(III), 0.023M in chromium(II), and 0.815 M in perchloric acid, by discarding the first part of the product band eluted from the ion exchange column. The spectrum of the product shows maxima at 568 nm (ϵ , 23.9) and 414 nm (ϵ , 21.0). In a number of other cases with cobalt(II) present the maxima were at the same positions but the apparent extinction coefficients were about 5% higher. The chromium(III) product was hydrolyzed at 50°C to give $\text{Cr}(\text{OH}_2)_6^{3+}$ as identified by its visible and ultraviolet spectrum with maxima at 572 nm (ϵ , 13.2), 408 nm (ϵ , 15.2), and 255 nm (ϵ , 6.6).

The spectrum of the chromium(III) product of the reduction is typical of other chromium(III) carboxylate complexes shown in Table 12, and is assumed to be



If the carbamate ligand were N-bonded it would be expected to have a spectrum similar to $(\text{OH}_2)_5\text{CrNH}_3^{3+}$,⁵¹ and possibly to hydrolyze to the amine complex as well.

Isocyanatopentaamminecobalt(III)

The kinetics of the reduction were studied as a function of hydrogen ion and chromium(II) concentrations. The

Table 12

ELECTRONIC SPECTRAL DATA FOR CHROMIUM(III) CARBOXYLATE
COMPLEXES

Complex	λ_{max} nm	ϵ_{max}	λ'_{max} nm	ϵ'_{max}	Ref.
$(\text{OH}_2)_5\text{CrO}_2\text{CH}^{2+}$	575	20.2	412	21.1	a
$(\text{OH}_2)_5\text{CrO}_2\text{CCH}_3^{2+}$	570	24.4	410	22.2	b
$(\text{OH}_2)_5\text{CrO}_2\text{CNH}_2^{2+}$	568	23.9	414	21.0	c
$(\text{OH}_2)_5\text{CrO}_2\text{CCH}_2\text{CO}_2\text{CH}_3^{2+}$	567	23.9	412	22.0	d
$(\text{OH}_2)_5\text{CrO}_2\text{CC}_6\text{H}_4\text{CN}^{2+}$	570	21.5	410	22.7	c
$(\text{OH}_2)_5\text{CrO}_2\text{C(O)CH}_3^{2+}$	555	19.9	410	21.0	e

^a From $(\text{NH}_3)_5\text{CoO}_2\text{CH}^{2+} - \text{Cr}^{2+}$ reaction. J. R. Ward and A. Haim, J. Amer. Chem. Soc., 92, 475 (1970).

^b In H_2O ; E. Deutsch and H. Taube, Inorg. Chem., 7, 1532 (1968). In 10.4 M HClO_4 the extinction coefficients are 19.8 and 21.0.

^c In ~0.05 M HClO_4 and ~0.25 M NaClO_4 .

^d D. H. Huchital and H. Taube, J. Amer. Chem. Soc., 87, 5371 (1965).

^e H. J. Price and H. Taube, Inorg. Chem., 7, 1 (1968).

results are summarized in Table B-8 Appendix B. The concentration dependence of the rate is given by

$$-\frac{d \ln[(\text{NH}_3)_5\text{CoNCO}^{2+}]}{dt} = k_1[\text{Cr}^{2+}] + k_2[\text{H}^+]. \quad (\text{IV-12})$$

The results in Table B-8 give $k_1 = 0.51 \text{ M}^{-1}\text{sec}^{-1}$ and $k_2 = 0.162 \text{ M}^{-1}\text{sec}^{-1}$ at 25° in $1.0 \text{ M LiClO}_4 - \text{HClO}_4$, while at 10° $k_1 = 0.22 \text{ M}^{-1}\text{sec}^{-1}$ and $k_2 = 0.042 \text{ M}^{-1}\text{sec}^{-1}$.

It would seem most probable that the k_2 path, which is independent of chromium(II), represents a hydrolysis reaction. A study of the hydrolysis reaction has been completed as mentioned previously, and the reaction was found to produce $\text{Co}(\text{NH}_3)_6^{3+}$. However no $\text{Co}(\text{NH}_3)_6^{3+}$ has been found under the conditions used to study the kinetics of the reduction. It has also been found, as shown in Table 13, that one mole of chromium(II) is consumed for each mole of cobalt(III) even under conditions when the reaction proceeds 75% by the k_2 path.

The results of an ion exchange study of the chromium(III) products of the reduction are given in Table 14. The data in Table 14 indicate that at least 75% of the product is carbamatopentaaquochromium(III), either when the reaction proceeds 66% or 50% by the k_2 path. The chromium(III) product was identified by comparison of its visible spectrum to that of the product from reduction of $(\text{NH}_3)_5\text{CoO}_2\text{CNH}_2^{2+}$

Table 13

STOICHIOMETRY OF $(\text{NH}_3)_5\text{CoNCO}^{2+} + \text{Cr}^{2+}$ REACTION

$[\text{Cr}^{2+}]$ M ^a	$[\text{Co}^{3+}]$ M ^a	$[\text{H}^+]$ M ^a	$[\text{Cr}^{2+}]$ found after rxn M ^b	$[\text{Cr}^{2+}]$ used in rxn M ^c	% k_2 ^d path
0.0473	0.0095	0.070	0.0378	0.0095	30
0.0473	0.0095	0.106	0.0368	0.0105	40
0.0473	0.0095	0.373	0.0367	0.0106	75

^a Concentrations are initial values in M units.

^b Determined by adding excess 0.100 N Fe^{3+} after the reaction was complete, and determining the excess Fe^{3+} iodometrically with 0.100 N sodium thiosulphate.

^c Obtained by subtracting entry four from entry one.

^d Calculated using equation (IV-12) with $k_1 = 0.51 \text{ M}^{-1} \text{ sec}^{-1}$ and $k_2 = 0.162 \text{ M}^{-1} \text{ sec}^{-1}$.

Table 14

ION EXCHANGE ANALYSIS OF THE PRODUCTS FROM THE REACTION OF $(\text{NH}_3)_5\text{CoNCO}^{2+}$

WITH CHROMIUM(II) .						
$10^2 [\text{Cr}^{2+}]$ M^a	$10^2 [\text{Co}^{3+}]$ M^a	$[\text{H}^+]$ M^a	$(\text{OH}_2)_5\text{CrO}_2\text{CNH}_2^{2+}$ found, moles ^b	$\text{Cr}(\text{OH}_2)_6^{3+}$ found, moles ^b	% as $(\text{OH}_2)_5\text{CrO}_2\text{CNH}_2^{2+}$ ^c	% ₂ ^d path
8.32	5.14	0.267	0.556×10^{-4}	1.35×10^{-4}	72.2	50
8.32	5.14	0.504	0.583×10^{-4}	1.33×10^{-4}	75.7	66
4.48	5.21	0.267	0.606×10^{-4}	0.606×10^{-4}	77.5	66
4.48	5.21	0.267	0.605×10^{-4}	0.605×10^{-4}	77.4	66

^a Concentrations are initial values in molar units.

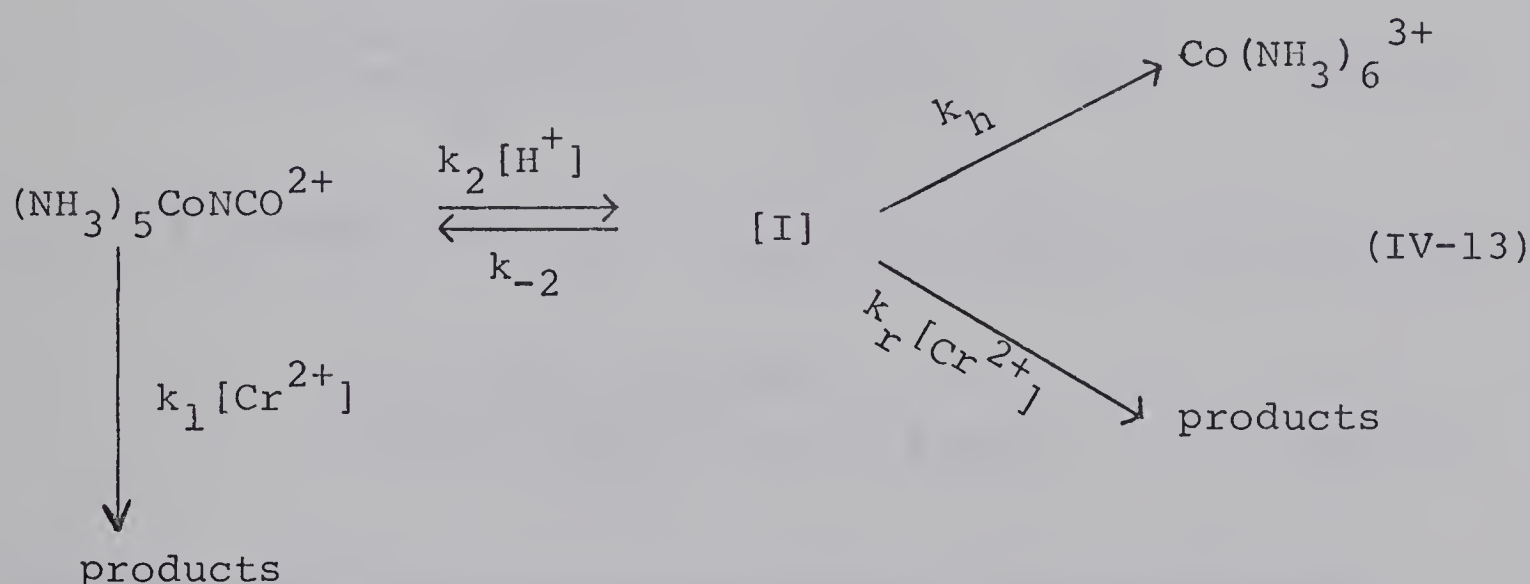
^b Determined as chromate

^c Based on total number of moles of cobalt(III) complex.

^d Calculated as noted in Table 13.

discussed previously. It seems likely that the 25% of product unaccounted for is hydrolyzed on the ion exchange column to give $\text{Cr}(\text{OH}_2)_6^{3+}$. The amount of $\text{Cr}(\text{OH}_2)_6^{3+}$ obtained from hydrolysis could not be determined since air oxidation of aqueous chromium(II) solutions yields much more $\text{Cr}(\text{OH}_2)_6^{3+}$ than the amount expected from reduction of the cobalt(III) complex.

The following reaction scheme will account for these observations under certain limiting conditions as discussed later.



If a steady state assumption is made for the concentration of the intermediate [I] then

$$- \frac{d \ln [(\text{NH}_3)_5\text{CoNCO}^{2+}]}{dt} = \frac{k_1 [\text{Cr}^{2+}] (k_{-2} + k_h + k_r [\text{Cr}^{2+}]) + k_2 [\text{H}^+] (k_h + k_r [\text{Cr}^{2+}])}{(k_{-2} + k_h + k_r [\text{Cr}^{2+}])} \quad (\text{IV-14})$$

If it is assumed that $(k_h + k_r[\text{Cr}^{2+}]) \gg k_{-2}$, then

$$-\frac{d \ln[(\text{NH}_3)_5\text{CoNCO}^{2+}]}{dt} = k_1[\text{Cr}^{2+}] + k_2[\text{H}^+] \quad (\text{IV-15})$$

Comparison of equation (IV-12) and (IV-15) shows that proposed reaction scheme is consistent with the observed rate law.

It should also be noted that when $[\text{Cr}^{2+}] = 0$, i.e. when only hydrolysis is being observed, then equation (IV-14) reduces to

$$-\frac{d \ln[(\text{NH}_3)_5\text{CoNCO}^{2+}]}{dt} = \frac{k_2 k_h}{k_{-2} + k_h} [\text{H}^+] \quad (\text{IV-16})$$

If it is assumed that $k_h \gg k_{-2}$, then equation (IV-16) gives

$$-\frac{d \ln[(\text{NH}_3)_5\text{CoNCO}^{2+}]}{dt} = k_2[\text{H}^+] \quad (\text{IV-17})$$

Therefore the rate constant obtained in the hydrolysis study should agree with the value of k_2 obtained from the reduction kinetics study. In fact the values are in good agreement being $0.162 \text{ M}^{-1}\text{sec}^{-1}$ at 25° from both studies and 0.046 (by interpolation) and $0.042 \text{ M}^{-1}\text{sec}^{-1}$ at 10° from the hydrolysis and reduction studies respectively.

The failure to observe any $\text{Co}(\text{NH}_3)_6^{3+}$ product under the kinetic conditions used must be due to a high ratio of k_r to k_h . The reaction scheme (IV-13), assuming steady

state conditions for [I] and also that $(k_h + k_r[\text{Cr}^{2+}]) \gg k_{-2}$, predicts that the product ratio

$$\left[\frac{[\text{Co}(\text{NH}_3)_6^{3+}]}{[\text{Cr}^{3+}]} \right]_{\infty} = \frac{k_2 k_h [\text{H}^+]}{\{k_2 k_r [\text{H}^+] + k_1 (k_h + k_r [\text{Cr}^{2+}])\} [\text{Cr}^{2+}]} \quad (\text{IV-18})$$

Rearrangement of (IV-18) gives

$$\frac{k_r}{k_h} = \frac{\frac{k_2 [\text{H}^+]}{[\text{Cr}^{2+}]} \left[\frac{[\text{Cr}^{3+}]}{[\text{Co}(\text{NH}_3)_6^{3+}]} \right]_{\infty} - k_1}{k_1 [\text{Cr}^{2+}] + k_2 [\text{H}^+]} \quad (\text{IV-19})$$

In a kinetic run with initial concentrations of Cr^{2+} , 0.032 M; H^+ , 0.20 M; $(\text{NH}_3)_5\text{CoNCO}^{2+}$, 1.38×10^{-3} M, an upper limit of 3×10^{-4} M was placed on the amount of $\text{Co}(\text{NH}_3)_6^{3+}$ product⁵⁴. Assuming that $[\text{Cr}^{3+}]$ equals the initial amount of $(\text{NH}_3)_5\text{CoNCO}^{2+}$, as indicated by the stoichiometry studies, then $k_r/k_h \gtrsim 60$. Since no build-up of intermediate was observed in the hydrolysis study it can be concluded that k_h is at least 5 times greater than the maximum value of $k_2[\text{H}^+]$ in the hydrolysis study. Therefore $k_h \gtrsim 5 (0.014) \text{ sec}^{-1}$ and $k_r \gtrsim 4.2 \text{ M}^{-1} \text{ sec}^{-1}$.

Pentaamminecobalt(III) Nitrile Complexes

The chromium(II) reduction of $(\text{NH}_3)_5\text{CoN}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{N}^{3+}$,

$(\text{NH}_3)_5\text{CoN}\equiv\text{CC}_6\text{H}_4\text{OH}^{3+}$, and $(\text{NH}_3)_5\text{CoO}_2\text{CC}_6\text{H}_4\text{C}\equiv\text{N}^{2+}$ was found to be independent of hydrogen ion concentration and obey the rate law

$$-\frac{d[\ln(\text{cobalt(III) complex})]}{dt} = k''[\text{Cr}^{2+}]. \quad (\text{IV-20})$$

The rate data for these complexes are given in Table B-9 of Appendix B. The rate constants and activation parameters are given in Table 15.

For the reduction of the terephthalonitrile complex ion exchange of the reaction mixtures after ten half-times yields only free terephthalonitrile and $\text{Cr}(\text{OH}_2)_6^{3+}$. For a reaction mixture 0.027 M in chromium(II), 0.0014 M in cobalt(III) complex, and 0.182 M in hydrogen ion, 96% of the ligand was recovered. The solutions were added to an ion exchange column and the first eluent through was collected and diluted in a volumetric flask. The amount of free terephthalonitrile was then determined by measuring the ultraviolet spectrum. The free ligand has a very characteristic ultraviolet spectrum with maxima at 235 nm (ϵ , 2.35×10^4), 246 nm (ϵ , 2.85×10^4), 282 nm (ϵ , 1.80×10^3), and 291 nm (ϵ , 1.77×10^3) in H_2O . The progress of the reduction was also followed by scanning the spectrum in the 270-300 nm region. The scans showed that only free ligand was produced. Also for runs where the entire spectrum was scanned (300 - 700 nm) nearly isosbestic

Table 15

KINETIC PARAMETERS FOR THE CHROMIUM(II) REDUCTION OF THE
 $(\text{NH}_3)_5\text{Co}^{3+}$ COMPLEXES OF TEREPHTHALONITRILE, 4-CYANOPHENOL,
AND 4-CYANOBENZOIC ACID

Ligand	Temp °C	k" $\text{M}^{-1}\text{sec}^{-1}$	ΔH^\ddagger kcal mole ⁻¹	ΔS^\ddagger eu
terephthalonitrile	15.0	0.671	5.5	-40
	24.8	0.920	$\pm 0.3^a$	$\pm 2^a$
	34.8	1.30		
4-cyanophenol	24.8	0.0296	11.1	-28
	34.8	0.0576	$\pm 1.0^a$	$\pm 3^a$
	44.8	0.102		
4-cyanobenzoic acid	24.8	0.161	8.6	-33
	34.8	0.266	$\pm 0.5^a$	$\pm 3^a$
	44.6	0.424		

^a
 Errors are estimated assuming a $\pm 5\%$ error on the rate constants.

behavior was observed. A complicating factor in the reaction is the conversion of $(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{CN}^{3+}$ to $(\text{NH}_3)_5\text{CoNH}\overset{\text{O}}{\text{C}}\text{C}_6\text{H}_4\text{CN}^{2+}$ even under acidic conditions (0.1 M HClO_4). This conversion was more facile in sodium acetate solution as noted in Chapters II and III. In order to obtain a pure sample of the terephthalonitrile complex the compound was subjected to cation exchange chromatography a second time using sodium chloride as the eluting agent. A good separation was achieved from the amido compound but some hydrolysis occurs on the ion exchange column. Therefore our cobalt terephthalonitrile complex contained some of the amido form. Although the chromium(II) reduction of $(\text{NH}_3)_5\text{CoNHC}(\text{O})\text{C}_6\text{H}_4\text{CN}^{2+}$ was not studied in detail a few runs were carried out to determine the best conditions for studying the reduction of the terephthalonitrile complex. The preliminary rate measurements on the amido complex indicated that the reduction rate increased with decreasing acid concentration. Assuming a first order dependence on cobalt(III) and chromium(II) the rate constants at $[\text{H}^+] = 0.203$ and 0.614 were 9.05×10^{-3} and $7.77 \times 10^{-3} \text{ M}^{-1}\text{sec}^{-1}$ respectively at 24.8° .

The chromium(II) reduction of the 4-cyanophenol complex yields $\text{Cr}(\text{OH}_2)_6^{3+}$ and a chromium(III) product which is eluted from the ion exchange column with the characteristics of a $2+$ ion. The latter has a visible

spectrum which shows maxima at 610 nm (ϵ , 16.0), 428 nm (ϵ , 20.2), and 246 nm (ϵ , 1.92×10^3). The ultraviolet spectrum of $\text{HOC}_6\text{H}_4\text{CN}$ shows a maximum at 246 nm (ϵ , 1.7×10^4) with shoulders at 270 and 280 nm. These shoulders are also observed in the spectrum of the chromium complex. The visible and ultraviolet spectrum and elution characteristics of the chromium(III) complex are consistent with the formulation $(\text{OH}_2)_5\text{CrOC}_6\text{H}_4\text{CN}^{2+}$. The yield of penta-aquochromium(III) phenol complex varies between 0 - 20% under different conditions. The results of an ion exchange analysis of a number of different kinetic runs and one run specifically used for ion exchange are given in Table 16. Each reaction mixture was allowed to proceed to completion and then charged onto a cation exchange column (Dowex 50W X-12). The first eluent through the column was collected and diluted to volume in a volumetric flask. The ultraviolet spectrum was measured and the concentration of free 4-cyanophenol determined at the 246 nm maxima.

The acid hydrolysis and chromium(II) catalysed aquation of the chromium(III) phenol complex was studied in order to determine whether the chromium(III) phenol complex results from ~20% ligand transfer or whether the entire reaction proceeds via ligand transfer, with the initial chromium(III) product hydrolyzing during the course of the reduction to produce free phenol. A more

Table 16

ION EXCHANGE ANALYSIS FOR LIGAND RELEASED IN THE REACTION
OF $(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{OH}^{3+}$ WITH CHROMIUM(II).

[Cobalt(III) Complex] $\times 10^3$, M	[Reductant] $\times 10^2$, M	$[\text{H}^+]$ M	Moles phenol found $\times 10^5$	% free phenol recovered
1.65	3.87	0.050	2.03	85 ^a
1.60	3.87	0.710	2.12	91 ^a
1.45	6.46	0.132	1.90	87 ^b
11.9	3.75	0.087	14.7	83 ^a

a

24.8°C

b

34.8°C

concentrated solution of the phenol complex was prepared by ion exchange separation, after 90 minutes, of a reaction solution initially containing 0.030 M Cr^{2+} , 0.028 M cobalt(III) complex, and 0.180 M H^+ . The green phenol complex was separated from $\text{Cr}(\text{OH}_2)_6^{3+}$ on the column with a solution 0.0025M in HClO_4 and 0.125M in NaClO_4 and finally eluted quickly with 0.05M HClO_4 and 0.25M NaClO_4 . It was noted qualitatively that approximately the same amount of phenol complex was obtained for runs at either low (0.09 - 0.18 M) or high (0.7 - 1.0 M) hydrogen ion concentration. Since the spectral changes accompanying hydrolysis with or without added chromium(II) are small an ion exchange technique was adopted. Solutions of the chromium(III) phenol complex and chromium(II) were equilibrated for various times and the amount of free phenol determined as previously noted. For $[\text{Cr}^{2+}] = 0.056 \text{ M}$, $[\text{H}^+] = 0.05 \text{ M}$, $[\text{Cr(III) phenol}] = 1.58 \times 10^{-3} \text{ M}$, ionic strength 1.0 M, and equilibration times at 24.8° of 45, 90, and 182 min, only $12 \pm 1\%$ of free phenol was recovered. Also, a solution of chromium(III) phenol complex was equilibrated at 45° in 0.1 M HClO_4 for 25 hours, after which the ion exchange procedure yielded 9% free phenol. Apparently the chromium(III) phenol complex is very unreactive over the time scale of the cobalt(III)-chromium(II) reaction and therefore an upper limit of ~20% is placed on the remote attack path with respect to the

outer-sphere path.

There was no evidence for a basic path in the reduction of the cobalt(III) complex even at an acid concentration of 0.05 M and the production of $(\text{OH}_2)_5\text{CrOC}_6\text{H}_4\text{CN}^{2+}$ must have resulted from the initial product $(\text{OH}_2)_5\text{CrOHC}_6\text{H}_4\text{CN}^{3+}$. The phenolic proton in the latter complex would be expected to be quite acidic and thus lead to the formation of the $2+$ ion.

The 4-cyanobenzoate complex yields the expected $(\text{OH}_2)_5\text{CrO}_2\text{CC}_6\text{H}_4\text{CN}^{2+}$ product which has a visible spectrum with maxima at 570 nm (ϵ , 21.5) and 410 nm (ϵ , 22.7). This is consistent with the spectra of other carboxylatopentaaquochromium(III) complexes. The product comprised 89% of the theoretically expected value (based on complete transfer of ligand). Blank experiments with benzoatopentaamminecobalt(III)-chromium(II) gave 95% $(\text{OH}_2)_5\text{CrO}_2\text{CC}_6\text{H}_5^{2+}$. The benzoatopentaaquochromium(III) ion has a visible spectrum which shows maxima at 565 nm (ϵ , 30.0) and 412 nm (ϵ , 27.3). It should be noted that in both the 4-cyanobenzoate and benzoate cases a good separation of the chromium(III) complex from $\text{Cr}(\text{OH}_2)_6^{3+}$ was not possible since the bands diffused together on the column. The same results were obtained for columns in both the hydrogen and sodium ion forms. The values given above for percent transfer of ligand during the reduction are based on the amount of free ligand eluted straight through the ion exchange column.

The amount of ligand was determined spectrophotometrically at the ultraviolet maxima. For 4-cyanobenzoic acid and benzoic acid the maxima are at 237 nm (ϵ , 1.94×10^4) and 272 nm (ϵ , ~ 1000) respectively.

The complete spectrum during the reduction of the 4-cyanobenzoate complex was also scanned. For $[\text{Cr}^{2+}] = 0.0056$, $[\text{cobalt(III) complex}] = 0.0016$, and $[\text{H}^+] = 0.197$ the spectra showed the growth of two peaks at 410 and 570 nm. Good isosbestic behavior was observed for the entire reaction with isosbestic points at 385, 436, 555, and 667 nm.

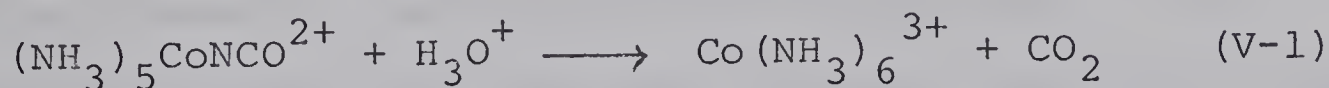
D I S C U S S I O N

Chapter V

1. Acid Hydrolysis of $(\text{NH}_3)_5\text{CoNCO}^{2+}$

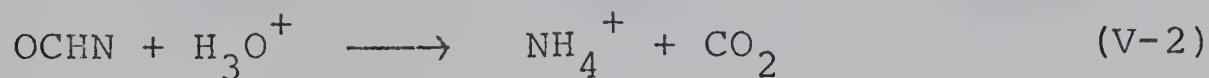
A number of publications have appeared recently on the preparation and bonding mode of cyanate, selenocyanate, and thiocyanate ions in various complexes.⁵⁵ The cyanate ion appears to be bonded to the metal ion through nitrogen in all its complexes except possibly for $\text{Re}(\text{OCN})_6^{2-}$, $\text{Re}(\text{OCN})_6^-$, $\text{Mo}(\text{OCN})_6^{3-}$,⁵⁵ and $(\text{C}_5\text{H}_5)_2\text{Ti}(\text{OCN})_2$.⁵⁷ All of the chemical and spectral data for $(\text{NH}_3)_5\text{CoNCO}^{2+}$ indicate that the cyanate ion is bonded through nitrogen.

The chemical evidence provides the strongest support for nitrogen bonding of cyanate. In acid solution the complex decomposes via the reaction



If the complex were oxygen bonded the product would be $(\text{NH}_3)_5\text{CoOH}_2^{3+}$. Ablov, Popova, and Samus⁵⁸ have prepared the dimethylglyoxime (DMG) cobalt(III) complexes $((\text{DMG})_2\text{Co}(\text{NCO})(\text{OH}_2))$ and $((\text{DMG})_2\text{Co}(\text{NCO})_2)^-$. These were observed to hydrolyze in aqueous acid to give $((\text{DMG})\text{Co}(\text{NH}_3)(\text{OH}_2))^+$ and $((\text{DMG})_2\text{Co}(\text{NH}_3)_2)^+$, presumably by a reaction analogous to (V-I).

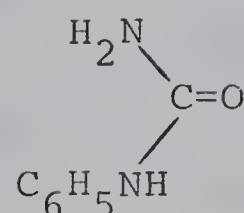
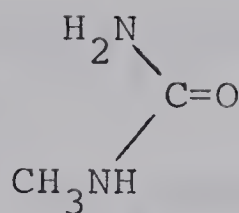
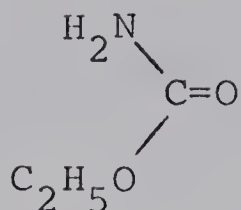
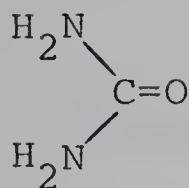
Jensen ⁵⁹ has studied the kinetics of decomposition of cyanic acid, and found for the reaction (V-2),



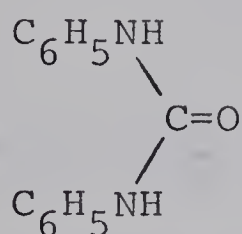
a rate constant of $1.2 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° (obtained by extrapolation) and ΔH^\ddagger of $15.1 \text{ kcal mole}^{-1}$. These results are in good agreement with the previous work of Lister.⁶⁰ The kinetic parameters for $(\text{NH}_3)_5\text{CoNCO}^{2+}$ are rather similar indicating that $(\text{NH}_3)_5\text{Co}^{3+}$ in the complex has a similar role to the hydrogen ion in HNCO.

The most unusual aspect of this work is the conversion of urea and several urea derivatives to the nitrogen bonded cyanate ligand. We had originally set out to prepare the C bonded urea compound but every preparation seemed to give the cyanato complex as a major product. The existence of the latter is not surprising,⁵⁸ and the compound has been made more directly from $(\text{C}_6\text{H}_5)_4\text{AsNCO}$ and $(\text{NH}_3)_5\text{CoOP}(\text{OC}_2\text{H}_5)_3^{3+}$ in dimethylsulfoxide.⁶¹ However, production of the cyanato complex from urea was quite unexpected.

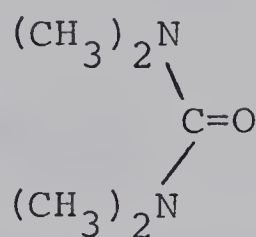
In order to explore the generality of this reaction and perhaps learn something of the reaction pathway, several urea derivatives have also been used as starting materials. The following were found to yield the cyanato complex as a product, using preparative methods (a) and (b)



However, under similar conditions no cyanate complex was obtained from

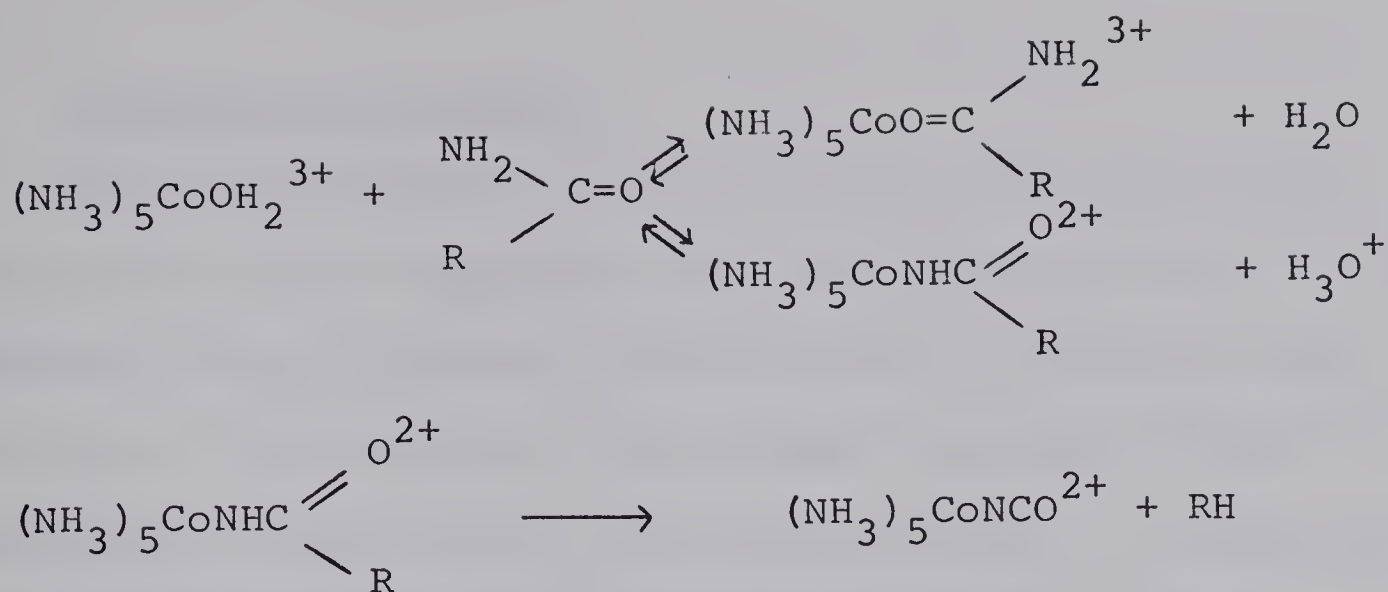


or



It should be noted that Fraser⁶² has reported that a preparation similar to (c) produces the N bonded urethane complex. Attempts to repeat Fraser's method, which starts with $((\text{NH}_3)_5\text{CoOH}_2)(\text{NO}_3)_3$, have yielded $((\text{NH}_3)_5\text{CoNO}_3)(\text{NO}_3)_2$, starting material and cobalt(II) species depending on the reaction time. It should also be noted that the chromium(II) reduction of $(\text{NH}_3)_5\text{CoNH}_2\text{CO}_2\text{C}_2\text{H}_5^{3+}$ would be expected to be slow in analogy to the formamide system whereas the rate reported by Fraser⁶² is large ($160 \text{ M}^{-1} \text{ sec}^{-1}$) and closer to the value for the chromium(II) reduction of $(\text{NH}_3)_5\text{CoNO}_3^{2+}$ ($\sim 90 \text{ M}^{-1} \text{ sec}^{-1}$) reported by Candlin, Halpern and Trimm.⁶³

The results of the preparative study reported here can be understood most easily in terms of the reactions



(where $\text{R} \equiv \text{NH}_2, \text{NHCH}_3, \text{NHC}_6\text{H}_5, \text{OC}_2\text{H}_5$)

Carbanilide and tetramethylurea may not produce the cyanato complex either because steric interactions make formation of the N bonded complex very unfavourable or because it would be necessary for phenyl or methyl groups to migrate. The fact that the O bonded isomer of urea has been isolated and does not seem to isomerize in solution or in the solid state indicates that O- to N- linkage isomerism is more likely to proceed by dissociation, as implied in the above reaction scheme, and not by intramolecular rearrangement.

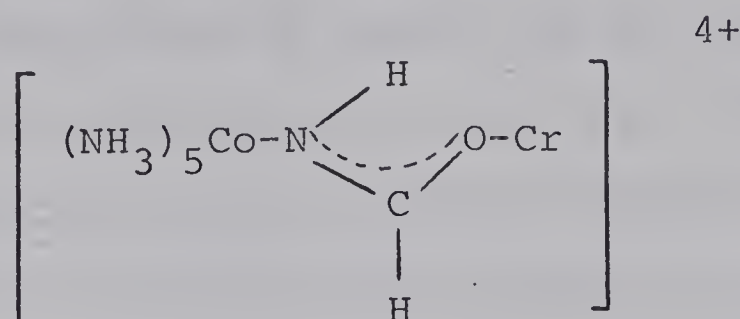
The reactions outlined above may provide a model for metal ion catalyzed decomposition of urea. The crucial feature is the formation of the N bonded urea complex which then forms the conjugate base of urea because the metal ion greatly increases the acidity of the coordinated $-\text{NH}_2$ protons. The conjugate base of urea then easily decomposes to cyanate and ammonia.

2. Chromium(II) Studies

The identification of the initial products of the reductions is most important in determining both the mechanism of the reaction and the point of attack of the reductant. The results of the product analysis of the chromium(II) reduction of the N-bonded isomer of formamido-pentaamminecobalt(III) do not prove conclusively the position of attack of the reducing agent on the formamide ligand. The possibility remains that the O-bonded chromium(III) product might have resulted from rapid linkage isomerization of an initial N-bonded chromium(III) product. The linkage isomerism might occur by internal rearrangement, or by chromium(II)-(III) electron transfer. The former mechanism seems rather unlikely in view of the stability of the pentaamminecobalt(III) linkage isomers, and the electron transfer mechanism would not be expected to be rapid, judging from the study of Deutsch and Taube⁴⁶ on acetatopentaquochromium(III) with chromium(II).

When the results from the O-bonded isomer of formamido-pentaamminecobalt(III) are considered, however, it becomes clear that attack at the atom directly bonded to cobalt(III) (oxygen in this case) does not occur. If attack at oxygen had occurred, then the chromium(III)-oxygen-bonded product should have resulted. However, this reaction produced only $\text{Cr}(\text{OH}_2)_6^{3+}$, probably by an outer-sphere mechanism.

It is concluded that the results from the O-bonded isomer rule out attack of chromium(II) on the atom bonded to cobalt(III). The product from reduction of the N-bonded isomer, $(\text{NH}_3)_5\text{CoNHCHO}^{2+}$, indicates that chromium(II) attack occurs at the formamide oxygen atom. The activated complex might be pictured as



This is analogous to the transition state (I) for adjacent attack as described in Chapter I.

The fact that the O-bonded formamide and DMF complexes are reduced without ligand transfer may be attributed to the nonavailability of a lone pair of electrons on the remote nitrogen atom. This lone pair may be necessary to form the bond to chromium(II) in the bridged activated complex. In the O-bonded complexes the nitrogen lone pair is drawn into the $\text{O}=\text{C}-\text{N}$ π system by the electron withdrawing $(\text{NH}_3)_5\text{Co}^{3+}$, and is therefore not available for bonding to chromium(II).

The observation that the conjugate base of the N isomer is reduced much more rapidly than its parent acid may provide a hint as to the electron transfer path. It might be argued that this rate enhancement is due to attack

by the reducing agent at the nitrogen lone pair in the conjugate base. However, this is contrary to the previous arguments and also does not explain why the O-bonded complexes are reduced without ligand transfer, since in the latter a lone pair is always available on the oxygen atom. Therefore, it seems that the greater rate of reduction of the conjugate base of the N isomer may be associated with the ability of the nitrogen to π -bond with the C=O system. This may provide more rapid electron transfer to the cobalt(III) or may provide a more stable radical ion intermediate, in which the electron is delocalized in the formamide π -antibonding system.

On the basis of the previous arguments it is predicted that electron transfer should not occur readily through an -NH_2 group. If the lone pair of electrons on the nitrogen is available for bonding to the reducing agent, then there will not be a π system in conjugation with the nitrogen lone pair of electrons. On the other hand, if the lone pair is part of a conjugated system then it will not be available for bonding to the reducing agent. It is assumed that the necessary conditions for bridged transfer are the presence of a non-bonding lone pair of electrons on the atom forming the bridge to the reducing agent, and a conjugated system between the bridging group atoms attached to the reducing agent and

the oxidizing agent. Therefore two non-sigma bonding pairs of electrons are required. Since an -NH_2 group has only one lone pair it cannot act as a bridging group. These predictions are consistent with the observations of Nordmeyer and Taube¹⁴ on the chromium(II)-nicotinamido-pentaamminecobalt(III) system and those of Hurst and Taube²⁵ on the chromium(II) reduction of (methylenamido-fumarato)pentaamminecobalt(III).

Also, the urea and N-cyanoguanidine complexes are both reduced by an outer-sphere mechanism as evidenced by the low specific rate constant, comparison to outer-sphere reduction of O-bonded formamide and N,N-dimethylformamide complexes, and failure to detect any chromium(III) product other than $\text{Cr}(\text{OH}_2)_6^{3+}$.

The fact that the cyanamide complex is only reduced through its conjugate base further supports the ideas outlined above. Removal of a proton from cyanamide gives the ligand $(\text{N}\equiv\text{C-NH})^-$, in which the N-H nitrogen has a free electron pair and another electron pair in conjugation with the rest of the ligand.

The carbamate system was studied in order to check the previous report⁶² that chromium(II) reduction gave an N-bonded chromium(III) product. This result clearly conflicts with predictions based on the proposed conditions for bridged transfer. It should be noted that the hydrogen

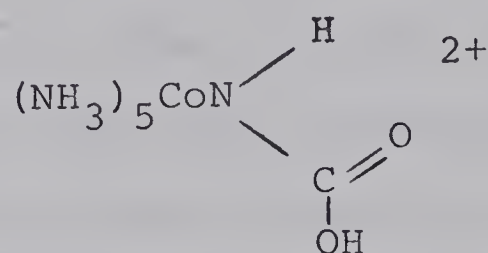
ion dependence of the rate law found in the present study is opposite to that reported in reference 62 since the rate shows closer to an inverse rather than direct dependence on hydrogen ion concentration. In addition no evidence has been found for an N-bonded chromium(III) product, either as a reactive intermediate or as the stable final product. Unless N- to O- bonded linkage isomerism is very fast it must be concluded that the carbamate complex is reduced through bridging to an oxygen of the carbamate ligand.

It is not possible to decide which of the two carbamate oxygens are involved in the bridge from these results. However, the results on the formamide complexes have shown that the carbonyl oxygen is the one used. The results on the urea complex support this proposal. Urea has a carbonyl oxygen directly bonded to cobalt and should not have any greater steric hindrance than the carbamate complex, yet the urea complex is reduced by an outer-sphere mechanism. Therefore an oxygen atom directly bonded to cobalt cannot act as a good bridging atom. This is also consistent with the work of Stritar and Taube²³ on the chromium(II) reduction of carboxylatopentaammineruthenium(III) complexes.

For the chromium(II) reduction of isocyanatopentaamminecobalt(III) the estimated value of the specific rate constant of $\sim 4.2 \text{ M}^{-1}\text{sec}^{-1}$ seems to be a reasonable

lower limit for chromium(II) reduction through a simple bridging group. The specific rates for chromium(II) reduction of the N bonded formamide and O bonded carbamate complexes are 1.7 and $2.4 \text{ M}^{-1} \text{ sec}^{-1}$ respectively at 25° .

The nature of the intermediate I in equation (IV-13) has not been specified but it seems most probable that the acid catalyzed hydration of the cyanate complex would yield



This could decompose to $\text{Co}(\text{NH}_3)_6^{3+}$ in acidic solution and the N-bonded carbamate could serve as a good bridging group for electron transfer.

It should be noted that the previous results for the simple amide bridging ligands would predict that the protonated form of the proposed intermediate, $(\text{NH}_3)_5\text{CoNH}_2\text{CO}_2\text{H}^{3+}$, would undergo slow reduction by chromium(II). It is therefore necessary to assume that the $-\text{NH}_2$ proton is quite acidic. This is not unreasonable in view of the fact that the analogous N-bonded formamide complex, $(\text{NH}_3)_5\text{CoNH}_2\text{CHO}^{3+}$, has a pK_a of approximately 2.2. The $-\text{CO}_2\text{H}$ group would be expected to increase the acidity of the carbamate complex relative to that of the formamide complex.

It should also be noted that a mechanism other than simple bridging is available for the k_1 path in the cyanate case. It is possible that the slow step in the reduction of $(\text{NH}_3)_5\text{CoNCO}^{2+}$ involves initial hydration of the coordinated cyanate by a water molecule in the hydration sphere of the chromium(II) ion. This would give a carbamate bridged intermediate in which facile electron transfer could occur to give $(\text{OH}_2)_5\text{CrO}_2\text{CNH}_2^{2+}$ as product. Admittedly this mechanism does not seem favourable compared to hydration by a free water molecule when reactant charges and the relative nucleophilicity of free and coordinated water molecules are considered. In any case, if hydration from the coordination sphere of another metal ion were operative then metal ions should catalyze the hydrolysis of $(\text{NH}_3)_5\text{CoNCO}^{2+}$ to $\text{Co}(\text{NH}_3)_6^{3+}$. However, no catalysis by aqueous copper(II) at pH 4 has been observed and therefore this type of hydration is not important in the electron transfer reaction with chromium(II).

It is concluded that the k_1 path for reduction of $(\text{NH}_3)_5\text{CoNCO}^{2+}$ involves a simple inner-sphere mechanism with $-\text{NCO}^-$ acting as the bridging ligand. The $(\text{OH}_2)_5\text{CrOCN}^{2+}$ formed initially must hydrate to give the observed product $(\text{OH}_2)_5\text{CrO}_2\text{CNH}_2^{2+}$.

Rate constants and activation parameters for the complexes already discussed are shown in Table 17 along with several other systems for comparison. It may be noted

Table 17

KINETIC PARAMETERS FOR CHROMIUM(II) REDUCTION OF SOME
 $(\text{NH}_3)_5\text{CoX}$ COMPLEXES

Complex	$k(25^\circ)$ $\text{M}^{-1} \text{sec}^{-1}$	ΔH^\ddagger kcal mole^{-1}	ΔS^\ddagger eu
$(\text{NH}_3)_5\text{CoOC}(\text{NH}_2)_2^{3+}$	1.9×10^{-2}	10.6	-31
$(\text{NH}_3)_5\text{CoOCHNH}_2^{3+}$	8.5×10^{-3}	10.7	-32
$(\text{NH}_3)_5\text{CoOCHN}(\text{CH}_3)_2^{3+}$	6.7×10^{-3}	10.6	-33
$(\text{NH}_3)_5\text{CoNCNC}(\text{NH}_2)_2^{3+}$	2.9×10^{-2}	8.3	-37
$(\text{NH}_3)_5\text{CoNHCHO}^{2+}$	1.7	12.0	-17
$(\text{NH}_3)_5\text{CoO}_2\text{CH}^{2+} \text{ a}$	7.2	8.3	-27
$(\text{NH}_3)_5\text{CoO}_2\text{CNH}_2^{2+}$	2.4	11.4	-19
$(\text{NH}_3)_5\text{CoO}_2\text{CCH}_3^{2+} \text{ a, b}$	0.35	8.2	-33
$(\text{NH}_3)_5\text{CoN}_3^{2+} \text{ c}$	3×10^5	-	-
$(\text{NH}_3)_5\text{CoNCNH}^{2+}$	3.3×10^3	4.3	-28
$(\text{NH}_3)_5\text{CoNCS}^{2+} \text{ c}$	19	6.9	-29
$(\text{NH}_3)_5\text{CoNCO}^{2+}$	0.50	8.8	-30
$(\text{NH}_3)_5\text{CoO}_2\text{CC}_6\text{H}_5^{2+} \text{ a}$	0.153	9.0	-32
$(\text{NH}_3)_5\text{CoO}_2\text{CC}_6\text{H}_4\text{CN}^{2+}$	0.160	8.6	-33
$(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{OH}^{3+}$	2.96×10^{-2}	11.1	-28
$(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{CN}^{3+}$	0.920	5.5	-40
$(\text{NH}_3)_5\text{CoNC}_5\text{H}_4\text{CONH}_2^{3+} \text{ d}$	17.4	3.9	-40
$(\text{NH}_3)_5\text{CoNC}_5\text{H}_4\text{CONH}_2^{3+} \text{ e}$	3.3×10^{-2}	10	-31
	1.4×10^{-2}	9	-36
$(\text{NH}_3)_5\text{CoNC}_5\text{H}_5^{3+} \text{ f}$	4.0×10^{-3}	9	-39
$(\text{NH}_3)_5\text{CoFuOH}^{3+} \text{ g}$	1.32	6.7	-36

continued

Footnotes to Table 17

- a Reference 18.
- b The rate constant is for the acid independent path.
- c Reference 63.
- d Reference 14. The ligand is isonicotinamide.
- e Reference 14. The ligand is nicotinamide. The rate constant $3.3 \times 10^{-2} \text{ M}^{-1}\text{sec}^{-1}$ refers to the inner-sphere path whereas $1.4 \times 10^{-2} \text{ M}^{-1}\text{sec}^{-1}$ is for the outer-sphere path.
- f Reference 14.
- g Reference 25. Rate constant for the acid independent term.

that the ΔH^\ddagger and ΔS^\ddagger values are very similar for all the O-bonded systems which proceed without ligand transfer. This is not surprising perhaps, in view of the structural similarity of all of these ligands. The reduction of the N-cyanoguanidine complex has a significantly lower ΔH^\ddagger and more negative ΔS^\ddagger than that of the O-bonded systems. In terms of mechanism the values for the N-cyanoguanidine complex may be compared to those for the outer-sphere path for the nicotinamide system which also has a lower ΔH^\ddagger and more negative ΔS^\ddagger . However, the inner-sphere path for the latter system also has very similar activation parameters to the outer sphere path. It may be noted that ΔH^\ddagger and ΔS^\ddagger values, at least at 1.0 M ionic strength, are not necessarily greatly different for the systems which proceed with or without ligand transfer. It is clear that these parameters are not useful in distinguishing between inner- and outer-sphere chromium(II) reductions.

The reduction of the carbamate complex appears unusual in comparison to the acetate. The ΔH^\ddagger is higher, the ΔS^\ddagger more positive, and the latter is the dominant factor in making the reduction rate constant larger at 25°. The simplest argument would predict that carbamate is the more basic ligand, and therefore should form the most stable bridge to chromium(II), and have the lower ΔH^\ddagger , the opposite of what is observed. The high ΔH^\ddagger might be attributed to chelate formation between chromium(II) and the remote O and N atoms of carbamate. Electron transfer can occur through

chromium(II) reduction of $(\text{NH}_3)_5\text{CoN}_3^{2+}$ but the rate constant, $\sim 3 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° ,⁶³ indicates that the value of $3.3 \times 10^3 \text{ M}^{-1} \text{ sec}^{-1}$ observed for $(\text{NH}_3)_5\text{CoN}=\text{C}=\text{NH}^{2+}$ is not surprisingly large.

The rate constant obtained for the reduction of $(\text{NH}_3)_5\text{CoNCO}^{2+}$ (k_1) can be compared to that for other isoelectronic bridging ligands, azide, cyanamide anion, and thiocyanate. Table 17 shows that the ΔS^\ddagger values are remarkably constant, indicating a common mechanism. It has been noted by Burmeister and DeStefano⁶¹ that N-bonded cyanate is not likely to be a good bridging group because the negative charge of the ligand is largely localized on the nitrogen atom bonded to cobalt(III). Therefore, the oxygen atom will not be very basic and will not form a very stable bridge to the reducing agent. However, their conclusions were based on a molecular orbital calculation using only the pi-electron systems of some simple pseudohalide ligands and their hydrazides.⁶⁴ The data in reference 64 for the anions N_3^- , NCS^- , and NCO^- predicts that the order of basicity (of the N, S, and O atoms respectively) is $\text{N}_3^- > \text{NCS}^- > \text{NCO}^-$, and on this basis correctly orders the rates of electron transfer if formation of the bridge is important. However, similar calculations based on the acids show a reversed order ($\text{HNC}(\text{S}) > \text{HNC}(\text{O}) > \text{HNN}(\text{N})$) of basicity of the remote atom. Also, a correlation was noted between the differences in the pi-electron energies of the ions and their acids and

the strengths of the acids. However this correlation predicts that HSCN is a weak acid which is clearly not the case and leaves considerable uncertainty as to the applicability of the MO calculation.

It has been argued previously^{65,66} that the strength of the bridge to chromium(II) causes the difference in reactivity of the $-N_3$ and $-NCS$ complexes. This factor would generally seem to account for the rate trends with the additional $-NCNH$ and $-NCO$ complexes, and also for the fact that the rate differences are primarily due to ΔH^\ddagger differences, however no sound theoretical justification can be offered for the trend.

The pentaamminecobalt(III) complexes of terephthalonitrile, 4-cyanobenzoate, and 4-cyanophenol (nitrile-bonded) all have a potential site for remote attack of the reducing agent. In addition the 4-cyanobenzoate complex can react by the familiar adjacent attack path (through the carbonyl oxygen). For the terephthalonitrile and 4-cyanophenol complexes the remote $-C\equiv N$ and $-OH$ groups possess two non-sigma bonding pairs of electrons as well as being in conjugation with the rest of the ligand. This is also true of the carbonyl oxygen and the nitrile group in the 4-cyanobenzoate complex. There is also the possibility, of course, that the reactions will occur via an outer-sphere activated complex.

The terephthalonitrile complex is reduced with a high

specific rate constant ($0.92 \text{ M}^{-1}\text{sec}^{-1}$ at 25°) compared to the reduction of other nitrile complexes that are necessarily of the outer-sphere type. For example, the specific rate constant for the chromium(II) reduction of $(\text{NH}_3)_5\text{CoN}\equiv\text{C}-\text{CH}_3^{3+}$ is $0.017 \text{ M}^{-1}\text{sec}^{-1}$ at 25° .⁶⁷ On the other hand the malonodinitrile complex, $(\text{NH}_3)_5\text{CoN}\equiv\text{C}-\text{CH}_2-\text{C}\equiv\text{N}^{3+}$, which has a free nitrile group, is reduced at least 100 times faster than the acetonitrile complex. The high rate of reduction for the terephthalonitrile complex indicates that an inner-sphere rather than an outer-sphere reaction is occurring. However, ion exchange experiments have shown that the products of the reduction are free terephthalonitrile and $\text{Cr}(\text{OH}_2)_6^{3+}$.

If a normal outer-sphere reaction is ruled out on the basis of the large rate constant, then two possibilities remain, either inner-sphere remote attack at the nitrile group with fast hydrolysis of the resulting chromium(III) nitrile product, or outer-sphere reduction by a stepwise electron transfer to the ligand with the formation of a radical ion, and subsequent transfer to the oxidizing centre. The first possibility does not seem likely, since pentaquochromium(III) complexes are usually quite stable with respect to hydrolysis.⁶⁸ However, it should be noted that there have been no $(\text{OH}_2)_5\text{Cr}^{3+}$ nitrile complexes prepared to date. For the chromium(II) reduction of the isonicotinamide¹⁴ and fumarato²⁵ complexes a radical ion mechanism is thought to be operative. For these complexes

the inner-sphere path has been confirmed by isolation of the chromium(III) products. These reactions are characterized by a low enthalpy of activation and high negative entropy of activation (see Table 17). The activation parameters for reduction of the terephthalonitrile complex are very similar to those for the examples just mentioned and may indicate that a radical ion mechanism is also operative. If the reduction of the terephthalonitrile complex proceeds by the step-wise path then a comparison of the activation parameters with those obtained for the fumarato and isonicotinamide systems is only valid if formation of the precursor complex does not contribute to the enthalpy of activation.

The reducibility of the ligand is thought to play an important role in determining the detailed mechanism of the electron transfer, and those ligands which are easily reduced sometimes form complexes which are also easily reduced. The relationship between the reducibility of the ligand and its ability to undergo remote attack when complexed is however not a simple one.²⁴ Usually those complexes which are thought to be reduced by a radical ion mechanism involve ligands which are themselves easily reduced. Qualitative experiments indicate that the reduction of free terephthalonitrile by chromium(II) occurs only slowly over a period of weeks. However, it should be noted that the terephthalonitrile radical has been prepared by electrolytic reduction in N,N-dimethylformamide,⁶⁹ and

thus the radical ion may also be formed during the electron transfer.

As reported in the results section the reduction of $(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{OH}^{3+}$ by chromium(II) proceeds approximately 20% with ligand transfer and 80% without ligand transfer to chromium. This is quite surprising since the inner-sphere path must occur by remote attack and the ligand, 4-cyanophenol, would be very difficult to reduce. In fact Rieger ⁶⁹ et al attempted the polarographic reduction of 4-cyanophenol in N,N-dimethylformamide but could observe no radical formation. At the first polarographic wave, bubbling at the cathode was observed suggesting evolution of hydrogen and formation of the phenolate ion. At the second wave a cloudy gray solution was produced but no resonance was detected.

For the path that proceeds with ligand transfer the reducibility of the ligand would be expected to be important for both the radical ion and superexchange mechanisms. For a ligand which is difficult to reduce the reaction would be expected to be slow for both these mechanisms and might approach the outer-sphere limit. Both mechanisms are consistent with the data. For reduction of $(\text{NH}_3)_5\text{CoN}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{N}^{3+}$ and $(\text{NH}_3)_5\text{CoN}\equiv\text{CC}_6\text{H}_4\text{OH}^{3+}$ by a radical ion or superexchange mechanism one would expect that the terephthalonitrile complex would be much more easily reduced than the 4-cyanophenol complex since free terephthalonitrile is much easier

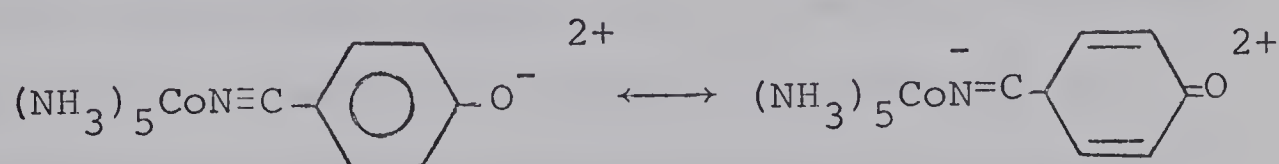
to reduce than 4-cyanophenol. The differences in the ΔH^\ddagger values given in Table 17 then may be simply a reflection of this fact.

If a double exchange mechanism were operative the reducibility of the ligand may not be a factor. For this mechanism the electron is transferred to the remote phenol group in the rate-determining step, and simultaneously an electron from the ligand is lost (in a fast step) to the oxidizing centre. Since the phenol is easily oxidized this type of mechanism may be favored over transmission of the reducing electron across the ligand to the cobalt(III) centre.

Unfortunately the rate constants and activation energies for the two paths could not be separated and the ΔH^\ddagger and ΔS^\ddagger values obtained shed little light on the question of the detailed mechanism. For the chromium(II) reduction of the isonicotinamido and nicotinamidopentaamminecobalt(III) complexes Taube and Nordmeyer¹⁴ concluded that the nicotinamide and isonicotinamide complexes were reduced by different mechanisms on the strength of a large difference in enthalpy of activation. However the difference can be rationalized in terms of the same mechanism (radical ion) since free nicotinamide is much more difficult to reduce than isonicotinamide, and this may contribute to the large ΔH^\ddagger difference found for the complex. If, on the other hand, the ΔH^\ddagger difference reflects a change in mechanism then the double

exchange mechanism may apply for the inner-sphere reduction of nicotinamidopentaamminecobalt(III). The double exchange mechanism may involve greater preparation at the oxidizing centre than the superexchange mechanism. This factor may contribute to a higher ΔH^\ddagger for double-exchange.

It was also shown in the results section that the rate of reduction of the 4-cyanophenol complex was independent of hydrogen ion concentration. The absence of a basic path for reduction is a reflection of the fact that the unprotonated complex



carries a negative charge which would be unfavorable for reduction of the ligand with respect to the protonated form. This observation also implies that formation of the precursor complex is not of major importance in this case because the phenoxide should form a much more stable complex than the phenol. Ligand reducibility appears to override any effect of precursor stability.

The acylation product, $(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{O}_2\text{CCH}_3^{3+}$, from reaction of $(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{OH}^{3+}$ with acetic anhydride, is reduced by chromium(II) with a specific rate constant of $0.042 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° .⁷⁰ This value is slightly higher than that obtained for the phenol complex and could reflect a modification of the reducibility of the ligand. It is likely that two paths operate in this system also

and ion exchange analysis of the products of this kinetic run did show that some free $\text{NCC}_6\text{H}_4\text{O}_2\text{CCH}_3$ was produced but the exact percentage is not known.

The results of the reduction of 4-cyanobenzoatopentamminecobalt(III) indicate that an inner-sphere reaction takes place with attack at the adjacent carbonyl oxygen. The activation parameters and rate are nearly identical to those obtained for the similar reduction of the benzoato complex¹⁸ and the same mechanism (adjacent attack at the carbonyl oxygen) is assumed to operate in both cases. In light of the conclusions reached for the reduction of the terephthalonitrile complex the change in mechanism for the 4-cyanobenzoate complex can be attributed to the increased difficulty in reducing free p-cyanobenzoate with respect to terephthalonitrile. The half-wave potentials for reduction in DMF are -2.53 and -1.97 volts respectively.⁶⁹

C O N C L U S I O N S

Chapter 6

For a number of the compounds studied complexation to $(\text{NH}_3)_5\text{Co}^{3+}$ has resulted in a change in the properties of the ligand. These changes can be understood in terms of the electron-withdrawing effect of the pentaamminecobalt(III) unit. For example, the change in the pK_a of the NH_2 protons upon complexation for the nitrogen bonded complexes of sulfamate³⁴ and formamide is >10 and >13 pK_a units respectively. The $(\text{NH}_3)_5\text{Co}^{3+}$ group also can influence remote groups and the pK_a of cyanamide is changed from 10 to 5 upon coordination. A smaller change has been observed for the remote OH group in the nitrile bonded 4-cyanophenol complex where the complex has a pK_a of 6.62 compared to 7.95 for the free ligand.

Changes in the pK_a of ligands upon complexation have also been observed for $(\text{NH}_3)_5\text{Ru}^{2+}$ complexes although the changes are not as large as those discussed previously. For the nitrile coordinated ruthenium(II) complexes of 2-, 3-, and 4-cyanopyridine the pK_a of the remote pyridine NH proton is increased by ~ 1 pK_a unit relative to the free ligand.⁷¹ This unexpected increase in basicity on coordination to $(\text{NH}_3)_5\text{Ru}^{2+}$ has been attributed to π back-donation of electron density from low-spin $(\text{NH}_3)_5\text{Ru}^{2+}$ to the ligand. This effect appears with Ru(II) because the reduced charge

on the metal atom favors back-donation to the ligand compared to Co(III) and Ru(III). Also for the complexes $(\text{NH}_3)_5\text{RuNCC}_6\text{H}_4\text{COOH}^{2+}$ and $(\text{NH}_3)_5\text{RuNCC}_6\text{H}_4\text{COOH}^{3+}$ the pK_a 's are 3.5 and 3.8 respectively compared to 3.6 for the free ligand.⁴² The effect of the $(\text{NH}_3)_5\text{Ru}^{2+}$ and $(\text{NH}_3)_5\text{Ru}^{3+}$ units on the remote carboxylate group is smaller and the pK_a is little affected.

For the nitrile coordinated $(\text{NH}_3)_5\text{Co}^{3+}$ complexes of terephthalonitrile, 3- and 4- cyanophenol, and 4-cyanobenzaldehyde a change in reactivity towards hydrolysis of the nitrile group to the amide group has also been observed. Hydrolysis of a nitrile to an amide usually requires concentrated acid or base, and elevated temperatures, however for the complexes, hydrolysis occurs easily at room temperature with dilute base. Apparently the nitrile carbon atom is more susceptible to nucleophilic attack in the complex due to the electron-withdrawing effect of the pentaamminecobalt(III) unit.

It has been found that the chromium(II) reduction of the conjugate base of formamidopentaamminecobalt(III) proceeds by attack at the uncomplexed C=O oxygen atom via an inner-sphere mechanism. Reduction through the acid form of the complex, $(\text{NH}_3)_5\text{CoNH}_2\text{CHO}^{3+}$, does not occur to any appreciable extent. The inner-sphere path clearly is observable because of the change in the acidity of the NH_2 protons due to the influence of the pentaamminecobalt(III).

For the oxygen bonded complexes of formamide N,N-dimethylformamide, urea, and dimethylsulfoxide⁷² the reduction proceeds without ligand transfer. Thus attack at the coordinated oxygen atom, although sterically possible, does not occur. This result, combined with the fact that reduction of $(\text{NH}_3)_5\text{CoNHCHO}^{2+}$ resulted in the formation of a stable oxygen-bonded pentaquochromium(III) complex, indicates that the chromium(II) reduction of pentaamminecobalt(III) carboxylato complexes,¹⁸ $(\text{NH}_3)_5\text{CoO}_2\text{C-R}^{2+}$, proceeds by attack of the reductant at the carbonyl oxygen atom and not at the coordinated oxygen. This conclusion is also supported by the fact that the carbamate complex reduction produces $(\text{OH}_2)_5\text{CrO}_2\text{CNH}_2^{2+}$ whereas the reduction of the sterically similar urea complex does not produce an oxygen-bonded urea product.

The observation that ligand transfer does not occur on reduction of O-bonded formamide, N,N-dimethylformamide, urea, and N-cyanoguanidine shows that attack of chromium(II) at a ligand NH_2 group is not a favourable process. This may be understood in relation to the fact that attack can occur at a ligand C=O oxygen atom if it is assumed that the atom attached to chromium(II) in the transition state must have two lone pairs of electrons. One of these is used in bonding to the reducing agent while the other is potentially part of a π conjugated system on the ligand. This proposal also explains the fact that remote attack is observed for

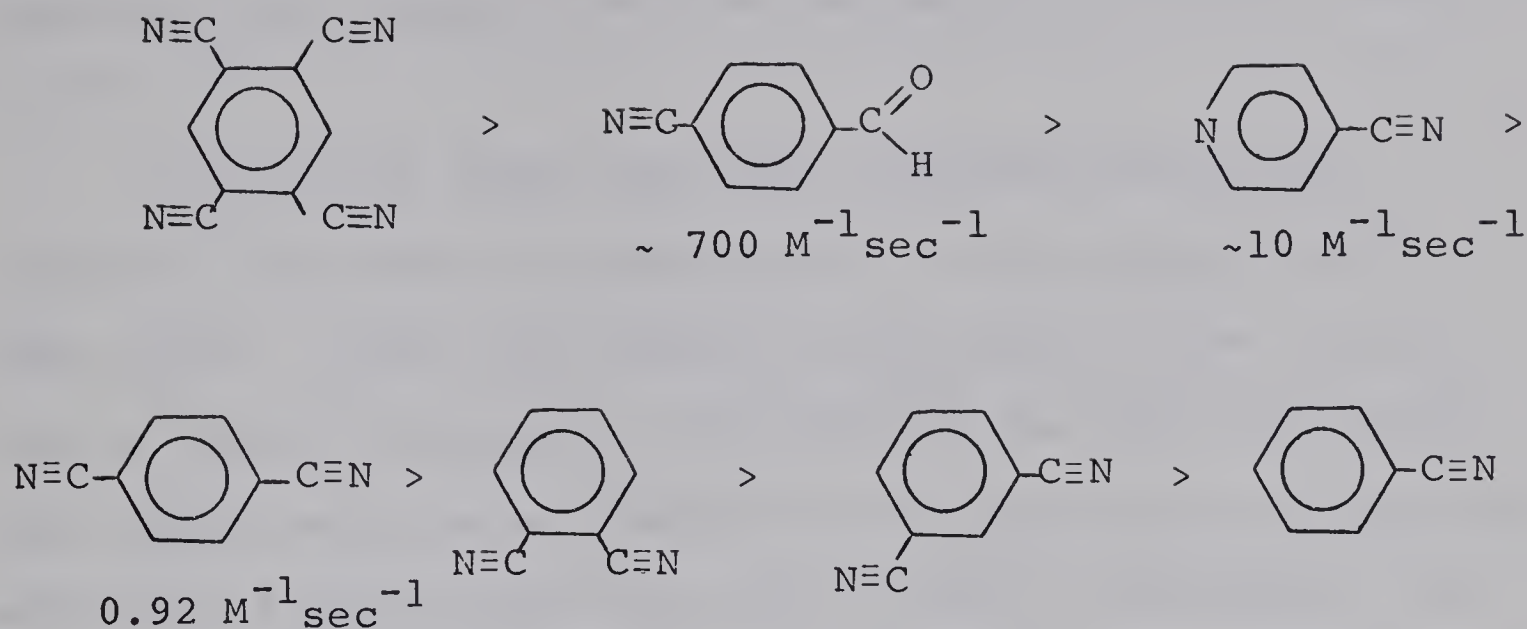
the conjugate base of cyanamide, $\text{N}\equiv\text{C}-\text{NH}^-$, since the NH group has two lone pairs. These principles may be important in biological redox processes in that they rule out electron transfer through both free or complexed NH_2 groups, which are abundantly present in amino acids and peptides.

It should be noted that the results in Table 17 indicate that the ΔH^\ddagger and ΔS^\ddagger for reactions with or without ligand transfer are not necessarily different. However, it does appear that the outer-sphere reactions have $\Delta H^\ddagger \sim 11$ kcal mole⁻¹ and $\Delta S^\ddagger \sim -30$ eu. If values much different from these are observed it would appear safe to conclude that simple outer-sphere reduction is not occurring.

It cannot be overly emphasized that a complete analysis of the products of the reduction is the best method to determine whether a reaction proceeds by an inner-sphere mechanism. For example, the reduction of the 4-cyanophenol complex has kinetic parameters which could be associated with an outer-sphere reaction and the small inner-sphere path would go undetected without a product analysis. For cases where the product analysis is not conclusive a classification into inner- or outer-sphere can sometimes be inferred from the rate law and rate constant. The cyanamide system is a case in point. Although the product found was $\text{Cr}(\text{OH}_2)_6^{3+}$ an inner-sphere mechanism was favored because the rate law contained an inverse hydrogen ion term and the reduction rate was extremely fast, with ΔH^\ddagger of 4.3 kcal

mole⁻¹, properties not expected for an outer-sphere path.

For the 4-cyanobenzoate, 4-cyanophenol, and terephthalonitrile complexes the reducibility of the ligand seems to be the factor which determines the mechanism and position of attack. In the case of the terephthalonitrile complex the activation parameters suggest that a radical ion mechanism may be involved. In this context the radical may be formed by remote attack at the C≡N or by a step-wise (outer-sphere) electron transfer to the ligand.⁷³ Since the product of the reduction was $\text{Cr}(\text{OH}_2)_6^{3+}$ the latter possibility is favored. For reduction of complexes with the aryl nitriles, and with other nitriles that possibly involve a radical ion (eg. $(\text{NH}_3)_5\text{CoNCC}_6\text{H}_4\text{CHO}^{3+}$), the rates and activation parameters for electron transfer may be related to the energy of the lowest unoccupied orbital on the ligand. This energy has been shown^{74,75} to be related to the polarographic half-wave potential for reduction for a series of related compounds. The following compounds are listed in order of decreasing ease of reducibility as judged from the polarographic half-wave potential for reduction as determined in N,N-dimethylformamide.⁶⁹ Also listed below each compound is the rate for reduction by chromium(II) of the nitrile coordinated pentaamminecobalt-(III) complex where it is known. For this series all the ligands except benzonitrile could react via a remote path.



In addition all of the nitrile complexes could be reduced by a step-wise outer-sphere process as described previously. For both cases the benzonitrile complex must be reduced by a normal outer-sphere reaction where direct transfer from the reductant to the oxidant takes place. This is necessitated by the fact that there are no remote lone pairs available for binding the reductant and also by the difficulty in reducing benzonitrile. At the present time only the terephthalonitrile complex has been thoroughly studied and work on the isophthalonitrile and 4-cyanobenzaldehyde complexes is in progress in this laboratory. The 4-cyanobenzaldehyde complex and the analogous amide have been synthesized and characterized. Preliminary stopped-flow measurements of the reduction of the 4-cyanobenzaldehyde complex by chromium(II) allows a first estimate of the rate as $\sim 700 \text{ M}^{-1} \text{sec}^{-1}$ at $[\text{H}^+] = 0.1 \text{ M}$, $\mu = 1.0$ (LiClO_4) and $\sim 29^\circ$. Work on the 4-cyanopyridine complex is complicated by non-linearity in the kinetic plots, however the

specific rate constant has been estimated as $10^{-1} \text{ M}^{-1} \text{ sec}^{-1}$ at 25° .⁷⁶

It should be noted that the proposed correlation neglects the effect of complexation on the properties of the ligand. Since the chemical properties of the ligands can be greatly altered by complexation the reducibility of the ligand may also be changed so that any such correlations with free ligand properties may be purely fortuitous. In fact, the reactivity of maleic and fumaric acids towards reduction by polarographic means⁷⁷ and by vanadium(II)⁷⁸ are not greatly different whereas the chromium(II) reduction of the pentaamminecobalt(III) complex of maleate⁷⁹ is faster by more than two orders of magnitude than the reduction of the fumarato²⁵ complex.

However, if the correlation with half-wave potentials does prove valid it would provide evidence for the radical ion mechanism as well as indicating strongly that the ligand π orbitals are involved in the electron transfer. For the ligands discussed electrolytic reduction in anhydrous, N,N-dimethylformamide has produced stable radicals and the possibility remains that the radical ion may be produced by chromium(II).

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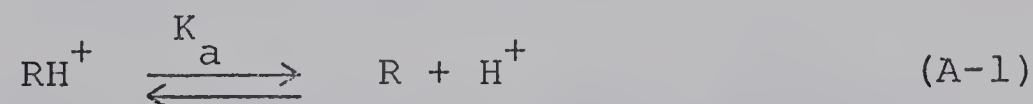
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A P P E N D I X A

DETERMINATION OF EQUILIBRIUM CONSTANTS SPECTROPHOTOMETRICALLY

For reactions of the general type



the equilibrium constant K_a is given by

$$K_a = \frac{[\text{R}][\text{H}^+]}{[\text{RH}^+]} \quad (\text{A-2})$$

From a consideration of the stoichiometry it is obvious that

$$C_T = [\text{RH}^+] + [\text{R}] \quad (\text{A-3})$$

where C_T is the total complex concentration. Substituting for RH^+ from (A-3) into (A-2) and rearranging, gives,

$$[\text{R}] = \frac{K_a C_T}{K_a + [\text{H}^+]} \quad (\text{A-4})$$

Now, according to Beer's law the absorbance of a solution is given by

$$A = \ell \epsilon_{\text{obsd}} C_T = \ell \epsilon_{\text{RH}} [\text{RH}^+] + \ell \epsilon_{\text{R}} [\text{R}] \quad (\text{A-5})$$

where ϵ_{obsd} is the molar extinction coefficient of the given solution as defined by (A-5) ϵ_{RH} and ϵ_{R} are the molar extinction coefficients of the protonated and unprotonated forms of R respectively, and ℓ is the optical path length in cm. Then substituting (A-3) into (A-5) one obtains

$$\ell \epsilon_{\text{obsd}} C_T = \ell \epsilon_{\text{RH}} C_T + \ell (\epsilon_R - \epsilon_{\text{RH}}) [R] \quad (\text{A-6})$$

and substituting (A-4) into (A-6) yields

$$\epsilon_{\text{obsd}} C_T = \epsilon_{\text{RH}} C_T + (\epsilon_R - \epsilon_{\text{RH}}) \frac{K_a C_T}{K_a + [H^+]} \quad (\text{A-7})$$

Rearranging and collecting terms finally gives

$$(\epsilon_{\text{obsd}} - \epsilon_{\text{RH}}) [H^+] = (-K_a) \epsilon_{\text{obsd}} + \epsilon_R K_a \quad (\text{A-8})$$

Equation (A-8) has the form of the equation $y = mx + b$ and a plot of $(\epsilon_{\text{obsd}} - \epsilon_{\text{RH}}) [H^+]$ versus ϵ_{obsd} yields a straight line with slope $(-K_a)$ and intercept $(\epsilon_R K_a)$.

For the case where the extinction coefficient of the base form (R) is better known than ϵ_{RH} , (A-7) may be rearranged differently to give

$$\frac{(\epsilon_{\text{obsd}} - \epsilon_R)}{[H^+]} = \left(-\frac{1}{K_a}\right) \epsilon_{\text{obsd}} + \frac{\epsilon_{\text{RH}}}{K_a} \quad (\text{A-9})$$

In this case a plot of $(\epsilon_{\text{obsd}} - \epsilon_R) [H^+]^{-1}$ versus ϵ_{obsd} yields a straight line with slope $-K_a^{-1}$ and intercept ϵ_{RH}/K_a .

A P P E N D I X B

TABLE B-1

EQUILIBRIUM DATA FOR THE SPECTROPHOTOMETRIC DETERMINATION OF
THE DISSOCIATION CONSTANT OF $(\text{NH}_3)_5\text{CoNH}_2\text{CHO}^{3+}$ at 25.5° .^a

Wavelength nm	$[\text{H}^+]$ M	ϵ_{obsd}^b $\text{cm}^{-1} \text{ M}^{-1}$	$[\text{H}^+](\epsilon_{\text{obsd}} - \epsilon_{\text{RH}})$ cm^{-1}
318.4	-----	87.3 ^c	-----
	0.0015	80.3	0.0761
	0.0030	72.7	0.1293
	0.0045	67.7	0.1715
	0.0075	59.2	0.2220
	0.0100	54.8	0.2520
	0.0151	49.0	0.2929
	0.0201	45.0	0.3095
	0.0301	40.8	0.3371
	0.9230	29.6	-----
	3.80	29.0 ^d	-----
366.4	-----	67.6 ^c	-----
	0.0015	60.0	0.0477
	0.0030	55.1	0.0807
	0.0045	51.2	0.1035
	0.0075	45.7	0.1313
	0.0100	43.0	0.1480
	0.0151	39.0	0.1631
	0.0201	36.4	0.1648
	0.0301	34.1	0.1776
	0.9230	28.2	-----
	3.80	27.7 ^d	-----

(continued)

Footnotes to Table B-1

- a Ionic strength $\mu = 0.92\text{M}$ (LiClO_4).
- b Based on total complex concentration of 0.0018M in a 5 cm cell.
- c Value determined in 0.92M LiClO_4 was identical to that determined at pH 9.0.
- d Value at $\mu = 3.80\text{M}$ (HClO_4) agreed well with that at $\mu = 0.92\text{M}$ (HClO_4) considering the ionic strength change.
-

TABLE B-2

RATE DATA FOR THE HYDROLYSIS OF ISOCYANATOAMMINECOBALT(III) IN ACID SOLUTION^a

Temp °C	[HClO ₄] M	k _o x 10 ³ , sec ⁻¹	
		obsd	calcd ^b
5.0	0.087	2.47	2.52
	0.174	4.88	5.04
	0.217	6.60	6.29
15.0	0.052	3.98	4.06
	0.070	5.46	5.46
	0.087	6.60	6.59
	0.122	9.63	9.52
	0.174	13.1	13.6
25.0	0.021	3.27	3.40
	0.035	5.50	5.67
	0.052	8.80	8.42
	0.070	11.2	11.3
	0.087	14.4	14.1

^a For all runs ionic strength $\mu = 1.0M$ (LiClO₄)

^b Rate constants are calculated from the equation
 $k_{\text{calcd}} = k_1[H^+]$ for k_1 's given in Table 5, Chapter IV.

TABLE B-3

KINETIC DATA FOR THE REDUCTION OF THE OXYGEN-BOUND FORMAMIDE,
 N,N-DIMETHYLFORMAMIDE, AND UREA COMPLEXES OF PENTAAMMINECO-
 (III) BY CHROMIUM(II)^a

Ligand	[Oxidant]x10 ³ M ^b	[Reductant]x10 ² M ^b	[H ⁺] M ^b	Temp °C	k _{obsd} x10 ² M ⁻¹ sec ⁻¹
OCHNH ₂	2.00	3.17	0.208	26.0	0.83
	2.20	3.90	0.200	26.0	0.87
	1.43	3.90	0.207	26.0	0.85
	2.28	5.72	0.791	36.0	1.68
	2.00	3.71	0.149	36.0	1.51
	1.95	3.17	0.093	36.0	1.69
	2.35	3.90	0.303	36.0	1.48
	1.95	3.17	0.592	36.0	1.50
	2.04	4.45	0.805	36.0	1.59
	2.17	5.57	0.207	36.0	1.66
	2.00	3.71	0.149	46.0	2.96
	1.59	3.71	0.303	46.0	2.96
	2.37	3.71	0.860	46.0	2.96
OCHN(CH ₃) ₂	0.90	3.98	0.074	32.6	0.72
	1.80	2.14	0.961	32.6	0.75
	1.80	2.14	0.077	32.6	0.82
	1.90	2.30	0.961	44.6	1.60
	1.90	2.30	0.077	44.6	1.60
	1.80	2.14	0.077	54.1	2.63
	1.80	2.14	0.077	54.1	2.51
OC(NH ₂) ₂	2.07	3.32	0.240	24.6	1.93
	2.17	3.32	0.478	24.6	1.93
	2.05	3.32	0.764	24.6	1.93
	1.95	3.07	0.248	24.6	1.89 ^c

(continued)

TABLE B-3 continued

OC(NH ₂) ₂	2.05	3.32	0.240	34.8	3.45
	2.15	3.32	0.478	34.8	3.42
	2.19	3.50	0.240	45.0	6.46
	2.22	3.50	0.478	45.0	6.46

- a For all runs ionic strength $\mu = 1.0\text{M}$ (LiClO₄).
- b Concentrations are initial values in molar units.
- c This run was scanned over the range 300-600 nm and the rate constant determined at 531 nm.

TABLE B-4

KINETIC DATA FOR THE REDUCTION OF $(\text{NH}_3)_5\text{CONH}_2\text{CHO}^{3+}$ BYCHROMIUM(II)^a

Temp °C	[Oxidant] x 10 ² M ^b	[Reductant] x 10 ² M ^b	[H ⁺] M ^b	k _{obsd} x 10 ² M ⁻¹ sec ⁻¹
25.5	0.21	3.32	0.760	1.12
	0.19	3.70	0.750	1.27
	1.05	16.78	0.500	2.02
	1.05	16.78	0.405	3.10
	0.86	16.78	0.280	4.00
	0.86	15.10	0.250	4.60
	0.99	16.55	0.197	5.70
	1.06	16.55	0.190	6.14
	1.08	23.02	0.170	7.00
34.4	0.21	3.70	0.750	2.20
	0.22	3.70	0.475	3.86
	0.21	3.70	0.270	6.14
	0.22	3.70	0.198	8.00
	0.25	3.79	0.188	8.80
44.6	0.21	3.70	0.750	3.80
	0.21	3.39	0.475	5.89
	0.25	3.79	0.465	6.36
	0.21	3.39	0.270	10.20
	0.21	3.39	0.198	14.00

^a For all runs $\mu = 0.92\text{M}$ (LiClO_4).^b Concentrations are initial values in molar units.

TABLE B-5

KINETIC DATA FOR THE REDUCTION OF $(\text{NH}_3)_5\text{CoN}\equiv\text{C}-\text{N}=\text{C}(\text{NH}_2)_2^{3+}$ BY CHROMIUM(II)^a

Temp °C	[Oxidant] x 10 ³ M ^b	[Reductant] x 10 ² M ^b	[H ⁺] M ^b	k _{obsd} x 10 ² M ⁻¹ sec ⁻¹
24.6	1.57	3.00	0.248	2.92
	1.47	3.21	0.189	2.81
	1.47	6.42	0.200	2.86
34.8	1.48	3.32	0.248	4.63
	1.48	3.32	0.486	4.70
	1.48	3.32	0.724	4.70
43.8	1.51	3.21	0.189	6.79
	1.51	3.21	0.486	6.79
	1.51	3.21	0.189	6.79

^a For all runs $\mu = 1.0\text{M}$ (LiClO_4).^b Concentrations are initial values in molar units.

TABLE B-6

KINETIC DATA FOR THE REDUCTION OF $(\text{NH}_3)_5\text{CoNCNH}_2^{3+}$ BYCHROMIUM(II)^a

Temp °C	[Oxidant] x 10 ³ M ^b	[Reductant] x 10 ² M ^b	[H ⁺] M ^b	k _{obsd} M ⁻¹ sec ⁻¹
24.6	1.91	3.13	0.129	0.172
	1.91	3.13	0.248	0.092
	1.82	3.13	0.486	0.049
	1.92	3.13	0.772	0.033
34.8	1.82	3.21	0.129	0.379
	1.63	3.32	0.189	0.258
	1.60	3.32	0.248	0.206
	1.60	3.32	0.486	0.105
	1.60	3.32	0.724	0.071
43.8	1.92	3.13	0.129	0.791
	1.92	3.13	0.248	0.388
	1.92	3.13	0.486	0.205

^a For all runs $\mu = 1.0\text{M}$ (LiClO_4).^b Concentrations are initial values in molar units.

TABLE B-7

KINETIC DATA FOR REDUCTION OF $(\text{NH}_3)_5\text{CoO}_2\text{CNH}_2^{2+}$ BY CHROMIUM(II)^a

Temp °C	[Oxidant] x 10 ³ M ^b	[Reductant] x 10 ³ M ^b	[H ⁺] M ^b	k _{obsd} M ⁻¹ sec ⁻¹
25.8	1.94	21.9	0.815	0.305
	2.00	38.7	0.811	0.284
	2.00	38.7	0.811	0.298
	2.30	7.7	0.440	0.431
	2.40	7.7	0.440	0.435
	2.00	41.0	0.247	0.583
	2.20	8.2	0.223	0.663
	2.15	7.7	0.223	0.629
	2.70	7.9	0.157	0.855
	2.10	7.9	0.121	1.06
	2.45	8.3	0.121	1.12
	2.70	8.3	0.121	1.14
	2.45	8.3	0.097	1.07
	2.30	7.9	0.098	1.25
	1.27	7.1	0.078	1.33
	2.46	7.8	0.074	1.37
	1.42	5.3	0.065	1.32
	1.25	5.3	0.065	1.30
	1.32	5.3	0.052	1.52
	1.28	5.3	0.052	1.54
	1.00	4.1	0.051	1.55
15.0	2.38	33.0	0.769	0.146
	2.38	33.9	0.484	0.206
	2.48	33.9	0.246	0.330
	2.38	33.0	0.198	0.404
	2.30	16.5	0.123	0.560
	2.43	16.5	0.099	0.628

continued

TABLE B-7 (continued)

15.0	1.29	5.3	0.065	0.702
	1.36	5.3	0.052	0.786
8.0	2.49	33.0	0.769	0.078
	2.49	33.0	0.484	0.119
	2.49	33.0	0.248	0.202
	2.47	33.0	0.198	0.228
	2.47	33.0	0.103	0.368
	1.32	17.7	0.068	0.392
	1.32	17.7	0.055	0.461

^a For all runs ionic strength $\mu = 1.0$ (LiClO_4).

^b Concentrations are initial values in molar units.

Table B-8

KINETIC DATA FOR THE REDUCTION OF $(\text{NH}_3)_5\text{CoNCO}^{2+}$ BY CHROMIUM(II)^a

Temp °C	[Oxidant] $\times 10^3 \text{ M}^b$	[Reductant] $\times 10^2 \text{ M}^b$	$[\text{HClO}_4]$ $\times 10^2 \text{ M}^b$	$k_{\text{obsd}} \times 10^2$, sec ⁻¹ exptl	calc ^c
25.0	1.7	1.05	5.62	1.47	1.44
	1.7	1.05	5.62	1.47	1.44
	2.1	1.61	5.67	1.76	1.72
	2.0	1.61	5.67	1.76	1.72
	1.4	2.42	5.65	2.11	2.13
	1.4	2.91	5.58	2.31	2.36
	1.2	3.23	5.67	2.43	2.53
	2.0	3.88	5.56	2.94	2.84
	1.7	4.20	5.64	3.15	3.01
25.0	1.2	3.23	0.87	1.58	1.76
	1.5	3.23	3.27	2.24	2.14
	1.5	3.23	3.27	2.27	2.14
	1.2	3.23	8.01	2.89	2.95
	1.3	3.23	12.8	3.59	3.69
	1.4	3.23	19.9	4.78	4.84
	1.4	3.23	19.9	4.47	4.84
10.0	1.4	1.61	5.20	0.578	0.572
	1.7	1.50	5.59	0.533	0.565
	1.7	1.50	5.59	0.530	0.565
	1.8	3.00	5.57	0.856	0.894
	1.6	3.00	5.57	0.856	0.894
	1.7	4.50	5.56	1.22	1.22
	1.8	6.00	5.54	1.56	1.55

^a For all runs ionic strength $\mu = 1.0 \text{ M}$ (LiClO_4).

^b Concentrations are initial values in molar units.

continued

Footnotes to Table B-8 (continued)

^c Calculated from equation (IV-12) with $k_1 = 0.500 \text{ M}^{-1}\text{sec}^{-1}$, and $k_2 = 0.162 \text{ M}^{-1} \text{ sec}^{-1}$ at 25° , and with $k_1 = 0.22 \text{ M}^{-1} \text{ sec}^{-1}$ and $k_2 = 0.042 \text{ M}^{-1} \text{ sec}^{-1}$ at 10° . The activation parameters for k_1 are $\Delta H^\ddagger = 8.8 \text{ kcal mole}^{-1}$, $\Delta S^\ddagger = -30.4 \text{ eu}$, calculated from k_1 at 25° and 10° .

Table B-9

KINETIC DATA FOR THE REDUCTION OF THE PENTAAMMINECOBALT(III)
 COMPLEXES OF TEREPHTHALONITRILE, 4-CYANOPHENOL, and 4-CYANO-
 BENZOATE BY CHROMIUM(II) ^a

Ligand	[Oxidant] x 10 ³ M ^b	[Reductant] x 10 ² M ^b	[H ⁺] M ^b	Temp °C	k _{obsd} M ⁻¹ sec ⁻¹
Terephthalo- nitrile	0.44	1.56	0.867	15.0	0.673
	0.71	1.73	0.131		0.670
	1.08	3.20	0.246	24.8	0.922
	1.13	1.70	0.123		0.925
	0.42	1.60	0.867		0.922
	0.49	1.60	0.867		0.904
	0.49	1.62	0.867	34.8	1.34
	1.08	3.20	0.246		1.27
	1.27	1.66	0.243		1.30
4-Cyanophenol	1.60	3.87	0.710	24.8	0.0288
	1.65	3.87	0.050		0.0290
	1.20	4.85	0.219		0.0294
	1.30	6.46	0.132		0.0287
	1.75	3.23	0.723		0.0280
	1.75	6.46	0.124		0.0308
	1.55	4.85	0.132		0.0301
	1.45	6.46	0.132	34.8	0.0577
	1.44	6.20	0.614		0.0581
	1.48	2.70	0.134		0.0570
	1.87	2.70	0.134	44.8	0.102
	1.79	5.40	0.132		0.102
	1.22	2.87	0.757	24.8	0.155
	2.20	1.37	0.673		0.160
4-Cyanobenzoate	2.20	1.37	0.673		0.162
	2.20	2.74	0.144		0.162
	1.07	2.87	0.101		0.168

Table B-9 Continued

4-Cyanobenzoate	1.07	2.87	0.101	24.8	0.162
	1.89	2.97	0.197	34.8	0.271
	1.43	2.97	0.757		0.259
	1.52	2.97	0.197		0.271
	2.00	2.67	0.148		0.262
	1.77	2.97	0.197	44.6	0.417
	1.55	2.97	0.757		0.424
	1.76	2.97	0.197		0.424

^aFor all runs ionic strength $\mu = 1.0 \text{ M (LiClO}_4\text{)}$.

^bConcentrations are initial values in molar units.

A P P E N D I X C

LINESHAPE DATA FOR THE NH₂ PROTONS OF (NH₃)₅CoO₂CNH₂²⁺ AT
DIFFERENT TEMPERATURES. DATA OBTAINED AT 100 MHz IN

d₇-DMF (FIGURE 10)

Temp	Chemical Shift ^a	Intensity	Temp	Chemical Shift ^a	Intensity
°C	Hz	cm	°C	Hz	cm
30	519	0	0	535	0.4
	523	0.6		541	1.0
	527	1.8		543	1.5
	529	3.0		545	2.3
	531	6.2		547	4.0
	532	9.1		549	7.0
	533	12.5		550	9.7
	534	16.6		551	12.8
	535	17.5		552	15.1
	535	17.3		553	15.8
	536	13.9		553	15.6
	537	9.9		554	13.4
	538	6.0		555	10.4
	539	4.8		556	7.5
	541	2.5		557	5.3
	543	1.4		559	2.9
	547	0.2		563	1.0
	549	0		567	0.5

continued

Appendix C (continued)

-10	535	0	-15	560	6.3
	545	0.8		562	8.1
	549	1.3		564	9.4
	553	2.4		566	10.0
	555	3.3		568	9.0
	557	4.5		570	7.1
	559	6.3		572	5.7
	561	8.8		574	4.3
	563	10.7		576	3.2
	564	11.1		578	2.5
	566	10.5		582	1.3
	567	9.4		586	0.7
	569	7.1			
	571	5.1	-20	536	0
	573	3.7		546	0.3
	575	2.7		552	1.1
	579	1.5		556	2.2
	591	0		558	3.0
				560	3.8
-15	536	0		562	4.6
	546	0.6		564	5.2
	550	1.2		566	5.5
	554	2.4		568	5.7
	556	3.3		570	5.8
	558	4.5		572	5.9

continued

Appendix C (continued)

-20	574	6.2	-25	583	4.8
	576	6.2		585	5.8
	578	6.2		587	6.6
	580	5.9		588	6.9
	582	5.2		589	6.7
	584	4.2		591	5.9
	586	3.1		593	4.6
	588	2.4		595	3.5
	590	1.7		597	2.4
	596	0.5		599	1.7
	606	0		607	0.7
-25	553	0.5	-30	551	0
	561	2.2		561	0.8
	563	3.1		565	2.3
	565	4.2		567	3.5
	567	5.2		569	4.7
	569	5.7		571	5.6
	571	5.4		572	5.7
	573	4.8		573	5.7
	575	4.0		575	4.9
	577	3.7		577	4.1
	578	3.6		579	3.4
	579	3.7		581	3.0
	581	4.1		582	2.9

continued

Appendix C (continued)

-30	583	3.0	-40	580	5.9
	585	3.3		582	5.3
	587	4.2		584	4.2
	589	5.6		586	3.1
	590	6.3		588	2.5
	591	7.2		590	2.2
	592	7.7		591	2.0
	593	7.6		592	2.2
	595	6.6		594	2.5
	597	5.0		596	3.6
	599	3.5		598	5.3
	601	2.6		599	6.3
	603	1.9		600	7.3
	605	1.4		602	7.7
	611	0.6		603	7.4
	621	0		604	6.7
				606	6.2
-40	566	0.6		608	3.6
	568	1.0		610	2.6
	570	1.6		612	1.9
	572	2.4		614	1.4
	574	3.4		618	0.8
	576	4.8			
	578	5.9	-50	579	0.8
	579	6.0		581	1.3

continued

Appendix C (continued)

-50	583	1.8	-50	625	2.5
	585	2.3		627	2.0
	587	3.2		629	1.6
	589	3.8		639	0.5
	591	4.0			
	593	3.8			
	595	3.2			
	597	2.7			
	599	2.2			
	601	1.8			
	603	1.6			
	605	1.7			
	607	2.3			
	609	3.2			
	611	4.2			
	613	5.1			
	614	5.5			
	615	5.4			
	617	4.9			
	619	4.3			
	621	3.6			
	623	3.0			

 a

With respect to internal TMS.

A P P E N D I X D

LINESHAPE DATA FOR THE NH_2 PROTONS OF $(\text{NH}_3)_5\text{CoOC}(\text{NH}_2)_2^{3+}$ AT
DIFFERENT TEMPERATURES. DATA OBTAINED AT 100 MHz IN $\text{d}_7\text{-DMF}$

(FIGURE 11)

Temp	Chemical Shift ^a	Intensity	Temp	Chemical Shift ^a	Intensity
°C	Hz	cm	°C	Hz	cm
30	670	0.3	30	704	1.7
	676	1.3		706	1.1
	678	1.7		710	0.3
	680	1.6		712	0
	682	1.7			
	684	2.5	0	667	0
	686	4.3		677	0.5
	687	5.6		685	1.6
	688	7.7		687	2.3
	689	10.6		689	2.6
	690	13.2		691	3.0
	691	14.9		693	4.4
	692	13.6		695	7.9
	693	10.5		696	10.9
	694	7.9		697	14.1
	696	4.0		698	16.3
	698	2.2		699	14.9
	700	1.8		700	11.5
	702	1.9		701	8.1

continued

Appendix D (continued)

0	705	3.0	-18	723	1.0
	707	2.5		733	0
	709	2.0			
	711	1.2	-27	674	0
	715	0.6		686	1.6
	719	0		690	2.7
				694	4.5
-18	673	0		696	5.9
	683	0.8		698	7.4
	687	1.3		700	8.8
	691	2.7		702	10.2
	695	4.5		704	12.3
	697	5.4		706	14.0
	699	7.3		707	14.4
	701	10.2		708	14.1
	703	13.5		710	13.2
	704	14.1		712	11.4
	705	13.7		714	9.3
	706	11.8		716	7.4
	707	10.3		718	6.1
	709	7.3		720	5.1
	711	5.5		722	4.2
	713	4.5		726	2.7
	715	3.6		730	1.4
	719	1.9		740	0

continued

Appendix D (continued)

-36	671	0	-43	669	0
	679	0.5		677	1.2
	689	2.0		681	2.0
	693	3.0		685	3.2
	701	6.1		689	4.2
	702	6.5		693	5.2
	703	6.7		697	6.0
	704	6.9		701	6.2
	705	7.1		705	6.3
	706	7.2		709	6.2
	707	7.2		711	5.9
	708	7.2		713	5.4
	709	7.2		717	5.4
	710	7.2		721	5.5
	711	7.2		725	5.5
	712	7.1		729	5.5
	714	6.9		731	5.5
	717	6.4		735	5.2
	719	5.9		741	3.7
	723	4.8		745	2.8
	729	3.2		751	1.6
	735	2.1		757	0.8
	741	1.1		763	0
	752	0			

continued

Appendix D (continued)

-52	673	0	-52	755	1.6
	681	1.1		759	1.1
	685	2.1		771	0
	689	3.9			
	691	5.0	-65	675	0
	693	5.8		681	0.7
	695	5.9		687	2.4
	697	5.7		691	3.7
	701	4.7		693	4.9
	705	3.7		695	6.8
	709	3.5		697	9.0
	713	2.8		698	9.4
	717	2.4		699	9.2
	721	2.3		701	7.8
	725	2.6		703	6.0
	731	3.7		705	4.6
	735	5.1		709	3.7
	737	5.7		711	3.1
	739	6.2		715	1.9
	740	6.3		721	1.4
	741	6.2		727	1.4
	743	5.7		731	1.5
	747	4.0		735	2.3
	751	2.7		739	3.9

continued

Appendix D (continued)

-65	741	4.9
	743	6.3
	745	8.1
	746	8.9
	747	8.7
	749	7.6
	751	6.3
	753	5.0
	757	3.3
	763	1.9
	771	0.8
	777	0

a

Chemical shift with respect to internal TMS

B29980